

On the Structures of Solid Rare Earth Oxalates and Malonates

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Lund 1973

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Printed in Sweden
Studentlitteratur
Lund 1973

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INTRODUCTION

About twenty publications dealing with the crystal structures of complexes formed in the solid state between the trivalent rare earth ions and multidentate carboxylate ligands have been presented in the series "Structural Studies on the Rare Earth Carboxylates". The results arrived at concerning the complexes ML_3^{3-} , where L is one of the tridentate ligands dipicolinate or oxydiacetate, have been summarized by Albertsson,¹ and the present paper is a summary of the results of the study of the compounds $M_2L_3 \cdot nH_2O$ formed by the bidentate ligands oxalate and malonate. The structural studies involved have been reported in the following communications

5. The Crystal and Molecular Structure of Neodymium(III) Oxalate 10.5-hydrate.²
13. The Crystal and Molecular Structure of Tetra-aquo Tris-oxalato Discandium(III) Dihydrate.³
16. The Crystal and Molecular Structure of Tetra-aquo Tris-oxalato Dytterbium(III) Dihydrate.⁴
17. The Crystal and Molecular Structure of Hexa-aquo Tris-malonato Dineodymium(III) Dihydrate.⁵
18. The Crystal and Molecular Structure of Hexa-aquo Tris-malonato Dineodymium(III).⁶
19. The Crystal and Molecular Structure of Penta-aquo Tris-malonato Dieuropium(III) Trihydrate.⁷
20. The Crystal and Molecular Structure of Mono-aquo Hydroxo Malonato Scandium(III) Monohydrate.⁸
21. On the Positions of the Water Molecules in Hexa-aquo Tris-oxalato Dineodymium(III) 4.5-hydrate at $-50^\circ C$.⁹

A preliminary account of the neodymium-oxalate structure was given in a short communication in 1968.¹⁰

The original interest in the structures of solid lanthanoid carboxylates arose during the study of the thermodynamic properties of the corresponding complexes in solution. When attempts are made to describe the results of such thermodynamic measurements on a microscopic level i.e. in molecular terms, it is valuable to know the structures of some related solid compounds, even though great care must be taken when comparing results obtained in the solid state with those arrived at in solution because of the very different interaction between the complex and its surroundings in the two different states.

The aim of the crystallographic investigation was to determine the the coordination numbers, the coordination bond lengths and the shape of the coordination polyhedra of the various complexes and also to study how the ligands are bonded i.e. whether a potential multidentate ligand acts as a chelate or not, and to determine the conformation of the ligands. By investigating structures of complexes formed by a given ligand with different rare earth ions, it is also possible to study the influence of the lanthanoid contraction on these properties.

The accuracy obtainable in the positions of the light atoms in structures containing metal ions as heavy as the lanthanoids is usually fairly low even when single crystal diffractometry data are used,^{11,12} and the variations in the ligand geometry caused by the lanthanoid contraction are often too small to be settled. The trivalent scandium ion has a similar outer electron shell configuration to the trivalent lanthanoid ions but a considerably smaller ionic radius. The decrease in ionic radius through the lanthanoid series is 0.21 Å while that between the smallest lanthanoid ion, Lu(III), and Sc(III) is 0.12 Å.¹³ Thus, a possible distortion of the ligand caused by the change in size of the central ion might be detectable in the comparison of a complex of

one of the largest lanthanoid ions and a corresponding Sc(III) complex. In addition, the lower atomic number of Sc(III) permits a higher precision in the determination of the dimensions of the organic ions. These are the reasons for including a scandium oxalate and a scandium malonate structure in the present work.

The formation of rare earth oxalate and malonate complexes in solution has been studied by Grenthe and coworkers.¹⁴⁻¹⁷ They found that a maximum of four oxalate ions are coordinated to the lanthanoids while the corresponding number of malonate ions is three. The five-membered chelate ring of the oxalate complexes is more stable than the six-membered ring of the malonate complexes. The latter complexes are even so weak that the formation of a chelate must be questioned. The values of ΔH° and ΔS° for the formation of the malonates are almost constant through the lanthanoid series. It was not possible to obtain the corresponding data for the oxalates because of the very low solubility of the compounds $M_2(\text{oxalate})_3 \cdot nH_2O$.

The variations in thermodynamic quantities such as ΔH° and ΔS° for complexation reactions most often exhibit "breaks" in the middle of the lanthanoid series.¹⁸ This feature has frequently been interpreted in terms of changes in the hydration number of the lanthanoid ions and/or of the partially hydrated complexes.¹⁹⁻²³ Strong evidence for the occurrence of such changes in the complexes $M(\text{oxydiacetate})_3^{3-}$ and $M(\text{EDTA})^-$ is given by heat capacity data.^{24,25}

A corresponding decrease in coordination number was not found for the complexes $M(\text{oxydiacetate})_3^{3-}$ and $M(\text{dipicolinate})_3^{3-}$ in the solid state.¹ Possibly as a result of the ligand geometry they are nine-coordinate throughout the lanthanoid series. In solution there is an increased difficulty for these species to be formed as the radius of the central ion decreases.^{26,27} In accordance with

this a steric hindrance for the shrinkage of the coordination polyhedron was noted for the solid oxydiacetate complexes.

Bidentate ligands are stereochemically less "demanding" and will thus possess a larger freedom at the formation of a coordination-polyhedron. For complexes with ligands as malonate,¹⁷ maleinate,²⁸ tropolonate,²⁹ and glycolate³⁰ the observed differences in ΔH° and ΔS° between the light and the heavy lanthanoids are less pronounced than for complexes with polydentate ligands. Changes in hydration number have, however, been discussed also for "bidentate" complexes, and it is thus of interest to determine the coordination numbers of the various lanthanoid ions in the solid hydrated oxalate and malonate complexes.

In the determination of the structures of $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$ and $\text{Eu}_2(\text{C}_3\text{H}_2\text{O}_4)_3 \cdot 8\text{H}_2\text{O}$ evidence was found for the presence of disordered water included in voids in the structures. A similar situation was found in the lanthanoid dipicolinate compounds.³¹⁻³³ It seemed likely that these water molecules were disordered around a number of average positions rather than being distributed completely at random over the available space, and it was assumed that the water molecules might be fixed at these average positions at low temperature. In order to test this assumption and, if possible, to determine the "average" arrangement of the disordered water molecules in neodymium oxalate, the structure was studied at -50°C . The knowledge of such an average arrangement would give information of the structural function of the disordered water in structures of this type.

EXPERIMENTAL

The solubility of the lanthanoid oxalates $M_2Ox_3 \cdot nH_2O$ is very low and it is difficult to prepare crystals of good quality of these compounds. At least three methods of preparation have been reported in the literature. The three methods are described below and are denoted I, II and III in Table 1 which summarizes the results of the preparations made in the present work. The abbreviations for the investigated compounds used in the following text are also included in Table 1.

Method I. Wylie³⁴ studied the crystals of the decahydrates formed by precipitation at different rates and different temperatures. He found that the water content for the compounds formed with the lighter members of the lanthanoid series varied continuously with the temperature of formation ($10 \leq n \leq 11$) and concluded that these compounds must contain "interstitial" water. He also found that good crystals were formed by very slow precipitation in the temperature range $50 - 80^\circ C$. Following this result, a number of deca- and hexahydrates have been prepared in the following way. Dilute solutions of rare earth nitrate (10 mM) and oxalic acid (15 mM) were slowly added (5 ml/h) to a large amount of water (3 l) kept at constant temperature (see Table 1). The crystals precipitated were wellformed but fairly small, except for those of SCOX which were large enough for single crystal work.

Method II. Larger crystals were obtained by a method described by Weigel *et al.*³⁵ A boiling solution of 5 g oxalic acid in 100 ml 3 M sulphuric acid was saturated with the lanthanoid oxide and slowly cooled to $0^\circ C$. This method is complicated by the formation of the acid oxalate $H \cdot M \cdot Ox_2 \cdot 3H_2O$ for the elements Er and Tm, but for the other lanthanoids wellformed crystals are formed.

Table 1. Preparation methods and ranges of existence for lanthanoid oxalates and malonates of the composition $M_2L_3 \cdot nH_2O$.

Oxalates					
Composition	Preparation method	temp. ($^{\circ}C$)	Formed by the elements	Temp. range of formation using method III ($^{\circ}C$)	Denotation of investigated compound Ref.
$M_2L_3 \cdot 10H_2O$	II	100 - 0	Ce - Ho	Ho: 15-85	NDOX 2, 9
	I	50	Ce - Er	Er: 40-55	
$M_2L_3 \cdot 6H_2O$	I	90	Ho - Lu	Ho: > 85 Er: > 55	YBOX 4
	II	100 - 0	Yb, Lu	Tm: > 35	
	I	70	Sc	Yb: > 25 Sc: > 35	SCOX 3
$M_2L_3 \cdot 6H_2O +$ $ML \cdot HL \cdot 2H_2O$	II	100 - 0	Er, Tm		

Malonates prepared at room temperature

Composition	Formed by the elements	Denotation of investigated compound	Ref.
$M_2L_3 \cdot 8H_2O$ (type I)	Ce - Gd	NDO	5
$M_2L_3 \cdot 6H_2O$	Ce - Eu	NDH	6
$M_2L_3 \cdot 8H_2O$ (type II)	Eu - Lu	EUM	7
$M(OH)L \cdot 2H_2O$	Sc	SCM	8

Method III. A third method has recently been described by Watanabe and Nagashima.³⁶ They use a two-phase system, composed of an aqueous solution of the rare earth chloride and a benzene solution of dimethyloxalate. The system is kept at constant temperature and the oxalate diffuses into the aqueous

solution and slowly forms the solid $M_2Ox_3 \cdot nH_2O$. By systematically varying the temperature, they determined the temperature ranges of formation for various hydrates $M_2Ox_3 \cdot nH_2O$ with $M = Dy - Yb$, Y , and Sc . Their results for the hexa- and deca-hydrates are included in Table 1. It is seen that the results of the less systematical preparations made in the present work agree with those found by Watanabe and Nagashima. Below the lower temperature limits given in Table 1 the authors obtained a 18 - hydrate when $M = Ho - Yb$ or Y and an octahydrate when $M = Sc$.

The rare earth malonates were prepared in a more straightforward manner. Dilute water solutions prepared from the appropriate amounts of the lanthanoid chloride or scandium hydroxide, malonic acid and sodium hydroxide were slowly evaporated at room temperature. The compositions of the precipitated solids are given in Table 1. The octahydrates are of two different crystal structures, one for the lighter elements (type I) and another for the heavier elements (type II). With the lighter elements the octahydrate type I is formed in most cases but sometimes the hexahydrate is obtained. The hexahydrate is metastable with respect to the octahydrate type I at room temperature. The preparations with Sc resulted in a basic malonate.

The crystals of the octahydrate (type I) and those of the hexahydrate are of good quality and size while those of the octahydrate (type II) are in most cases too small for single crystal work. All attempts to prepare larger crystals of the latter hydrate by varying the conditions of crystal growth were unsuccessful

The oxalates and malonates investigated were analysed for M , H , and C . The analyses for C and H were performed at the Division of Analytical Chemistry, Chemical Center, University

of Lund.

The single crystal X-ray intensity data were collected by the equi-inclination photographic Weissenberg technique using either $\text{CuK}\alpha$ or $\text{MoK}\alpha$ radiation (see Table 2). The relative intensities were measured visually by comparison with a calibrated scale.

The intensity data were corrected for Lorentz and polarisation effects. Corrections for absorption were applied to the data for NDO, NDH, EUM, and to the low temperature data for NDOX. It is known that absorption errors usually affect the positional parameters insignificantly while the thermal parameters are more seriously affected.^{37,38} Since the magnitude of the temperature factors has not been used for any conclusions in those cases where the absorption effects are left uncorrected no serious disadvantage is introduced. The absorption correction applied to the EUM data was calculated using an approximate value of the linear absorption coefficient, μ , for Eu(III) . The value of $\mu_{\text{Eu(III)}}$ is very uncertain because of the proximity of $\lambda_{\text{CuK}\alpha}$ to the L_I absorption edge of Eu. The correction applied lowered the R-value from 0.12 to 0.09.

The unit cell dimensions were calculated from powder data taken in a Guinier Hägg focusing camera with a diameter of 80 mm. Lead nitrate was used as an internal standard. The observed powder patterns for the various oxalates are given in Appendix I, Table 1, while those of the investigated malonates are found in Refs. 5-8.

Table 2. Crystal data and some details of the refinement of the structures. M is the number of parameters refined, N the number of independent reflexions used and $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

Compound	Unit cell dimensions (Å, °)	Space group and Z	Radiation used and μ (cm ⁻¹)	Approximate crystal size (mm ³). The mounting direction is underlined	M	N	R	Range of standard deviations ($\times 10^3$ Å) σ_M σ_C σ_O
NDOX	a = 11.678(2) b = 9.652(2) c = 10.277(2)	$P 2_1/c$	MoK α 31	0.15 $\times$ <u>0.05</u> $\times$ 0.10	70	1357	0.095	1 19-27 16-59
NDOX -50°C		2	CuK α 371	0.10 $\times$ 0.10 $\times$ <u>0.30</u>	78	756	0.122	2 25-74 19-134
SCOX	a = 9.317(2) b = 8.468(2) c = 9.489(2)	$A \bar{1}$ 2	CuK α 44	<u>0.10</u> $\times$ 0.10 $\times$ 0.03	118	843	0.076	2 5-11 7-9
YBOX	a = 9.611(2) b = 8.457(2) c = 9.778(2)	$A \bar{1}$ 2	CuK α 238	0.05 $\times$ <u>0.05</u> $\times$ 0.02	67	828	0.114	2 16-25 12-35
NDO	a = 11.258(2) b = 12.602(3) c = 14.689(3)	Pbcn 4	MoK α 50	<u>0.22</u> $\times$ 0.13 $\times$ 0.13	67	1750	0.092	1 12-20 9-19
NDH	a = 11.210(2) b = 12.383(2) c = 13.696(3)	I 2/a 4	MoK α 55	0.10 $\times$ 0.09 $\times$ <u>0.20</u>	63	1730	0.085	1 11-26 8-17
EUM	a = 12.220(5) b = 8.100(3) c = 20.545(9)	Pnma 4	CuK α 443	<u>0.16</u> $\times$ 0.02 $\times$ 0.04	81	690	0.091	2 23-62 16-38
SCM	a = 6.278(1) b = 15.359(2) c = 7.773(1)	$P 2_1/n$ 4	CuK α 87	<u>0.10</u> $\times$ 0.02 $\times$ 0.04	100	779	0.081	2 7-11 5-8

DETERMINATION AND REFINEMENT OF THE STRUCTURES

The positions of the metal ions were in all structures determined from the vector maps of three-dimensional Patterson syntheses. For the structure of SCOX the peaks in these maps were so well resolved that the positions of all non-hydrogen atoms could be determined without difficulty. In the other structures the positions of the light atoms were deduced from the electron density maps of $(F_o - F_c)$ syntheses based upon the position of the metal ion in each case. The approximate positional parameters arrived at in this way, the temperature factors and the scale factors were refined by full-matrix least-squares refinement. The refinement was checked by finally calculating a $(F_o - F_c)$ synthesis. These final electron density maps showed for the scandium structures some broad maxima attributable to hydrogen atoms. For the other structures no peaks of any significance were observed. Hydrogen atoms were not included in any of the refinements.

Some details of the refinement together with crystal data of the compounds are collected in Table 2. The observed and finally calculated structure factors are for YBOX given in Appendix I, Table 2, while the corresponding data for the other structures are given in the respective communications.

The calculations were performed on the CDC 3600 computer in Uppsala (NDOX, SCOX) and on the UNIVAC 1108 computer in Lund. The programmes used were those briefly described in Ref. 1 p. 23.

THE INVESTIGATED STRUCTURES

Detailed descriptions of the structures are found in Refs. 2-9. In this section the packing and linking of the complexes will be

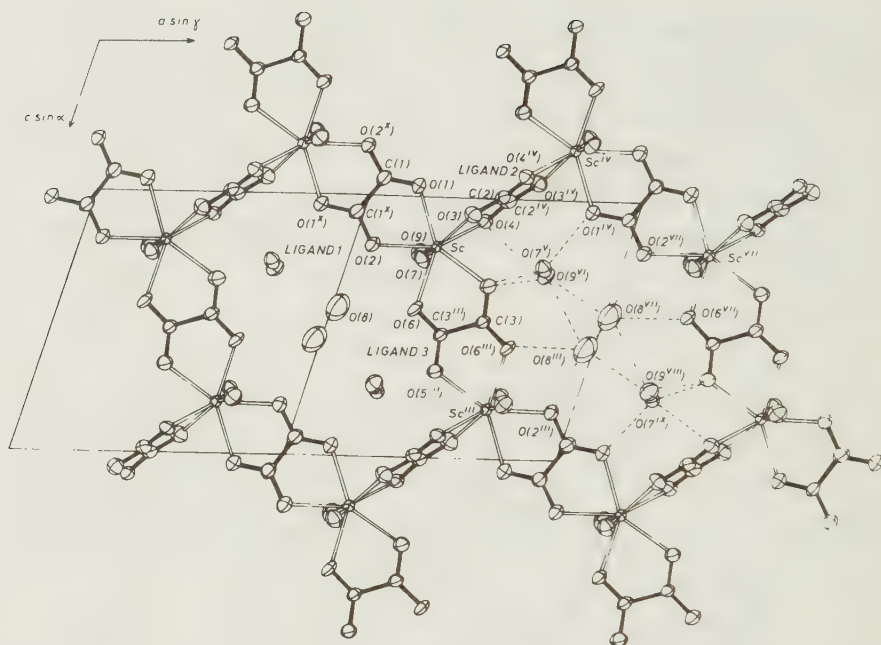


Fig. 2. SCOX. A part of the scandium-oxalate layer around $y = 0$ projected onto (010). The water oxygen atoms above and below the layer are included. Bonds within the oxalate ions are filled and metal-oxygen bonds are open. Possible hydrogen bonds are marked with dashes. Adjacent layers are related by the translation $(0, \frac{1}{2}, \frac{1}{2})$. The compounds SCOX and YBOX are isotopic.

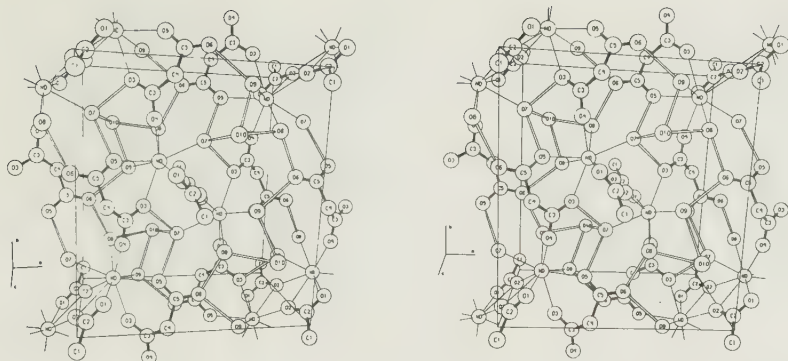


Fig. 3. NDO. A stereoscopic pair of drawings illustrating the neodymium-malonate network around $z = 0$. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1$, $-1/4 \leq z \leq 1/4$. Bonds within the malonate ions are filled, hydrogen bonds are open and metal-oxygen bonds are single lines. Adjacent networks are related by rotation around the two-fold axis passing through the methylene carbon C(1) and parallel with the y -axis.

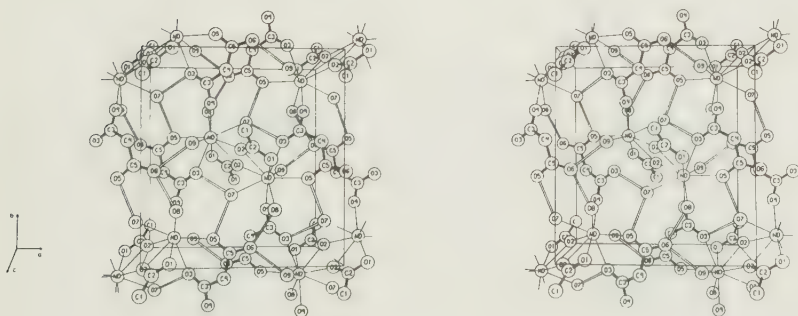


Fig. 4. NDH. A stereoscopic pair of drawings illustrating the neodymium-malonate network around $z = 0$. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1$, $-1/4 \leq z \leq 1/4$. The bonds are indicated in the same way as in Fig. 3. Adjacent network are related by rotation around the two-fold axis passing through the methylene carbon C(1) and parallel with the y -axis.

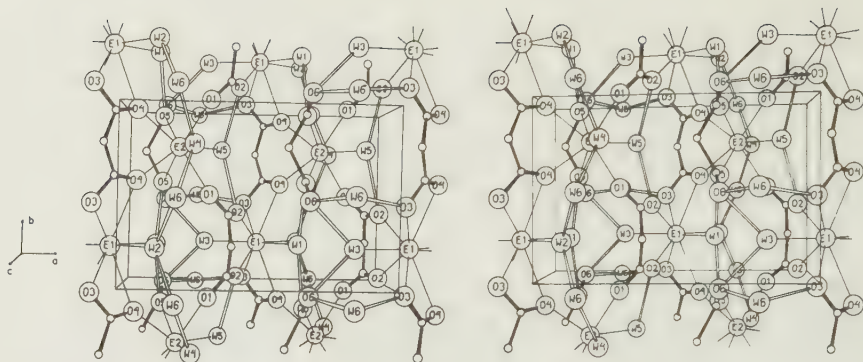


Fig. 5. EUM. A stereoscopic pair of drawings showing part of the europium-malonate layer around $z = 1/4$. The europium ions are denoted E 1 and E 2 and the water oxygens W 1, W 2 etc. The carbon atoms are small circles without notation. The bonds are indicated in the same way as in Fig. 3, and the box outlined is $-\frac{1}{2} \leq x \leq \frac{1}{2}$, $0 \leq y \leq 1$, $0 \leq z \leq \frac{1}{2}$. Adjacent layers are related by inversion through $(0, \frac{1}{2}, \frac{1}{2})$.

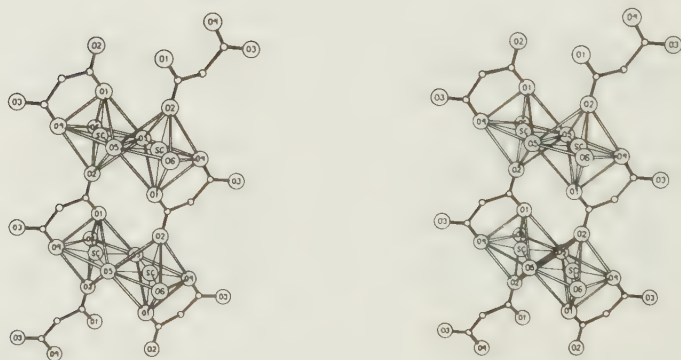


Fig. 6. SCM. A stereoscopic pair of drawings showing part of an infinite scandium-malonate chain. Bonds within the malonate ions are filled, metal-oxygen bonds are single lines and the edges of the octahedra are open. The carbon atoms are small circles without notation.

A carboxylate group may link two metal ions in several different ways. In the present structures the metal ions are linked by bridging carboxylate groups (Fig. 7 a) and/or by bridging-chelating carboxylate groups (Fig. 7 b). A bridging carboxylate group has each of its oxygens bonded to a separate metal ion, while in a bridging-chelating carboxylate group both oxygens are bonded to the same metal ion in a four-membered ring and one of the oxygens is also bonded to a second metal ion. The latter type of bridge is found in polymer lattices of complexes with high coordination numbers and seems to be a favourable way of achieving links and high coordination number, at the same time. The bond $M(1)-O(2)$ is in several cases considerably longer than $M(1)-O(1)$ and $M(2)-O(2)$ and it is sometimes difficult to decide whether a bond $M(1)-O(2)$ exists or if the position of $O(2)$ relative to $M(1)$ is merely decided by the packing of the complexes. A number of bond lengths for such bridges are collected in Table 3 to illustrate this feature.

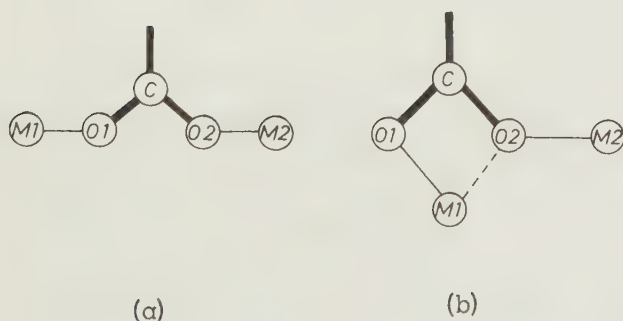


Fig. 7. The two types of carboxylate bridges formed in rare earth oxalates and malonates, (a) bridging carboxylate group, (b) bridging-chelating carboxylate group.

Table 3. Metal-oxygen bond lengths ($\text{\AA}$) for some bridging-chelating carboxylate groups. The numbering of the atoms is that used in Fig. 7 b. The organic ligands are abbreviated in the following way: malei: maleinate, fum: fumarate, imin: iminodiacetate, ac: acetate, nicot: isonicotinate.

Compound	M(1)-O(1)	M(2)-O(2)	M(1)-O(2)	Average M-O of the complex	Ref.
NDO	2.54	2.46	2.72	2.50	5
NDH	2.56	2.57	2.61	2.50	6
EUM	2.42	2.44	2.84	2.51	7
$\text{Nd}_2(\text{malei})_2\text{fum} \cdot 12\text{H}_2\text{O}$	2.48	2.43	3.06	2.51	39
$[\text{Nd}(\text{imin})(\text{H}_2\text{O})_3] \cdot \text{Cl}$	2.50	2.52	2.78	2.50	40
$\text{Ce}(\text{ac})_3 \cdot 0.7\text{H}_2\text{O}$	2.41	2.47	2.69	2.54	41
	2.61	2.56	2.58		
$\text{Pr}_2(\text{nicot})_6 \cdot 4\text{H}_2\text{O}$	2.43	2.43	2.87	2.53	42

Since bridging carboxylate groups are very common and are found in the majority of the compounds covered by the present series of lanthanoid carboxylate structures, it is of interest to examine the geometrical arrangement in such bridges. The situation around a number of bridging carboxylate groups is shown in Table 4 and in Fig. 8. The distances of M(1) and M(2) to the least-squares plane through the C-COO-group are denoted d_1 and d_2 , respectively. The quantity q is the ratio of the M(2)-O(2) bond length to the average M-O bond length of the actual complex.

For all the carboxylate groups involved O(1) is engaged in a five- or six-membered chelate ring and its geometrical situation is predominantly determined by the ring formation. The oxygen O(2) is regarded as an outer carboxylate oxygen of the complex around M(1). The plots of q versus the angle C-O(2)-M(2) (Fig. 8 a) and versus the distance d_2 (Fig. 8 b) show no correlation between q and C-O(2)-M(2) nor between q and d_2 . It can thus be concluded that large variations in the direction of the M(2)-O(2) bond with respect to the carboxylate group may occur without affecting the M-O bond length. This illustrates the great flexibility of the carboxylate bridge.

Table 4. Bond distances (Å) and angles (°) around some bridging carboxylate groups. The notation of the atoms is that indicated in Fig. 7 a. The ratio q is defined in the text. d_1 and d_2 are the deviations of M(1) and M(2) from the least squares plane of the C-COO-group, respectively. The organic ligands are abbreviated: glyc: glycolate, oac: oxyacetate, imin: iminodiacetate, tiodi: tiodiacetate.

Compound	M(1)-O(1)	$\angle_{M(1)-O(1)}$	M(2)-O(2)	$\angle_{M(2)-O(2)}$	Average M-O of the complex	q	d_1	d_2	Ref.
NDO	2.47	139	2.41	158	2.50	0.96	0.03	0.82	5
NDH	2.45	139	2.35	158	2.50	0.94	0.14	0.55	6
EUM	2.37	139	2.37	141	2.42	0.98	0.47	0.43	7
SCM	2.12	134	2.05	163	2.08	0.99	0.43	0.04	8
La(glyc) ₃	2.533	121	2.552	149		1.00	0.05	0.00	43
	2.525	124	2.444	149	2.55	0.96	0.05	0.03	
	2.584	124	2.580	149		1.01	0.20	0.25	
Gd(glyc) ₃	2.494	119	2.466	147		1.01	0.83	0.07	43
	2.417	123	2.353	147	2.45	0.96	0.16	0.02	
	2.438	125	2.447	155		1.00	0.12	0.75	
Eu(glyc) ₃	2.44	117	2.40	142		0.96	0.90	0.08	44
	2.53	122	2.45	143	2.51	0.98	0.44	1.35	
	2.41	122	2.47	138		0.98	0.64	1.32	
Er(glyc)(oac) · 2 H ₂ O	2.372	121	2.338	139		1.00	0.49	0.20	45
	2.328	131	2.378	142	2.34	1.02	0.30	0.12	
[Nd(imin)(H ₂ O) ₃]Cl	2.48	128	2.39	140	2.50	0.96	0.37	0.39	46
[Nd(tiodi)(H ₂ O) ₄]Cl	2.44	138	2.45	149	2.45	1.00	0.35	0.73	47

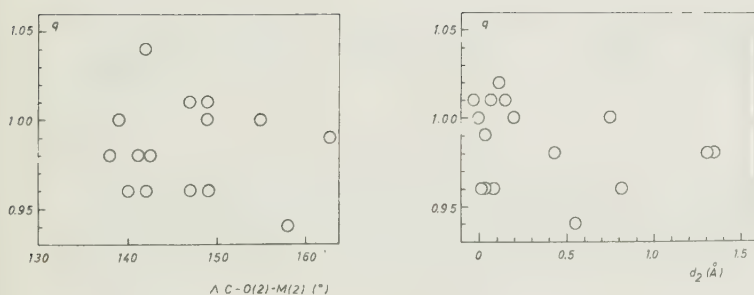


Fig. 8. A graphical survey of the variation of relative metal-oxygen bond length, q , with a) the angle C-O(2)-M(2) and b) the distance, d_2 , between the metal ion and the C-COO-plane.

In the oxalate compounds the complexes are all linked in layers by bridging carboxylate groups. (Figs. 1 and 2.) Each oxalate ion forms a five-membered chelate ring with one metal ion and an identical ring with an adjacent metal ion. Thus both its carboxylate groups are bridging between the same metal ions.

The less symmetrical malonate ion links the complexes in several ways. In NDO and NDH (Figs. 3 and 4) the complexes within the same layer are linked by one bridging group, $O(3)C(3)O(4)$, and by one bridging-chelating group, $O(1)C(2)O(2)$. The bridging group belongs to a malonate ion which forms a six-membered chelate ring with one of the neodymium ions. The bridging-chelating group is part of a malonate ion whose second carboxylate group is bonded to two neodymium ions in an adjacent layer. In EUM (Fig. 5) there are three crystallographically independent malonate ions, all within the same layer; one with bridging carboxylate groups, $O(1)C(1)O(2)$, a second with bridging-chelating carboxylate groups $O(3)C(4)O(4)$, and a third with its carboxylate groups bonded only to one metal ion, $O(5)C(5)O(6)$. The complexes in SCM are linked in chains by the bridging carboxylate group $O(1)C(1)O(2)$. (Fig 6.)

All the investigated complexes contain water molecules as ligands. These form hydrogen bonds both within the layers and between adjacent layers. These hydrogen bonds are the only bonds between layers in the oxalates and in EUM. Inter-layer hydrogen bonds are also formed in NDO and NDH but in these structures one malonate ion is bonded to neodymium ions of two adjacent layers.

The packing of the layers results, in all structures but NDH, in cavities between the layers filled out by additional water molecules. They may be definitely located forming hydrogen bonds

to the surrounding oxygens (NDOX: O(10), SCOX and YBOX: O(8), NDO: O(10), EUM: O(W 6), and SCM: O(7)), but sometimes there seem to be no fixed positions of these water molecules, which then can hardly be detected in the electron density maps (NDOX, EUM).

After this general survey of the structures, some features will be discussed more in detail, *viz.* the coordination polyhedra, the shape of the oxalate and malonate ions and finally the bonding situation of the water molecules.

THE COORDINATION POLYHEDRA

In the investigated structures the larger lanthanoid ions are coordinated by nine oxygens (NDOX, NDO, NDH, EUM) while the smaller lanthanoid ions are coordinated by eight oxygens (EUM, YBOX). The change of coordination number, CN, occurs at the elements Ho-Er for the oxalates and at the elements Eu and Gd for the malonates. The same decrease in CN was found for the solid lanthanoid complexes formed with the bidentate ligand glycolate.⁴⁸ With this ligand the change occurs at the elements Eu-Tb. The CN of Sc(III) is eight in SCOX and six in SCM.

Coordination numbers from six to ten have been established in lanthanoid compounds but nine and eight coordinate complexes are most commonly found. A survey of nine coordinate rare earth compounds containing oxygen and nitrogen as donor atoms is found in Ref. 1 p. 37 and a corresponding list of eight coordinate compounds is given in Table 5. These tables reveal a certain preference for CN = 9 for the larger lanthanoid ions, while CN = 9 seems to be as frequent as CN = 8 for the smaller ions.

Table 5. The metal-oxygen bond distances (Å) and the coordination polyhedra in eight-coordinate rare earth complexes. Organic ligands are abbreviated in the following way: acac: acetylacetonate, TTA: 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, bac: bensoylacetonate, DTA: diethylamine, pip: piperidine, HFA: hexafluoroacetylacetonate, glyc: glycolate, oac: oxyacetate.

Compound	Polyhedron	M-O		Ref.
		range	average	
La(acac) ₃ · 2 H ₂ O	BCTP	2.43-2.58	2.50	49
NH ₄ Pr(TTA) ₄ · H ₂ O	DOD	2.42-2.49	2.46	50
Nd(acac) ₃ · 2 H ₂ O	BCTP	2.38-2.56	2.47	51
Eu(acac) ₃ · 3 H ₂ O	BCTP	2.36-2.58	2.47	52
HEu(bac) ₄ · pip	SAP	2.33-2.42	2.39	53
HEu(bac) ₄ · DTA	SAP	2.36-2.43	2.39	53
EUM	SAP	2.37-2.48	2.42	7
HGd(bac) ₄ · pip	SAP	2.36-2.47	2.41	54
Ho(acac) ₃ · 4 H ₂ O	DOD	2.33-2.50	2.35	55
Y(acac) ₃ · 3 H ₂ O	SAP	2.30-2.46	2.35	56
CsY(HFA) ₄	DOD	2.31-2.35	2.32	57
Er(glyc)(acac) · 2 H ₂ O	DOD	2.24-2.48	2.34	45
Er(glyc) ₃ · 2 H ₂ O	BCTP	2.27-2.34	2.30	48
	SAP	2.28-2.37	2.32	
YBOX	DOD	2.28-2.41	2.34	4
SCOX	DOD	2.18-2.26	2.23	3

Among the 14 different ligands involved in the tables only the β-diketonates give CN = 8 in the beginning of the series.

In an analysis of molecular polyhedra of high coordination numbers given by Mutterties and Wright⁵⁸ it is pointed out that the energy barriers to changes of CN in rare earth compounds should be of the same order of magnitude as forces generated by packing and ordering factors in the solid state. This statement is in good agreement with the experimental findings that the change in CN occurs at different elements with different ligands (i.e. in different structures) and that with a given ligand both CN:s may exist for the same element, sometimes in the same structure (EUM).

Before entering into the discussion of the coordination polyhedra formed in the investigated structures, it is convenient to give a brief account of the types of polyhedra that might be expected.

Albertsson¹ has reviewed the present knowledge of the bonding in lanthanoid complexes and concludes that the bonding with good approximation may be regarded as purely electrostatic (ionic). Thus the structure of a hypothetical isolated complex is predominantly determined by the ligand-ligand repulsive forces and there are no pronounced directional bonds of the type found among the d-transition elements. Roughly speaking, a given complex will adopt a geometry where the coordinated ligand atoms are as far apart as possible, maintaining a constant distance to the central ion.

A number of articles⁵⁸⁻⁶¹ describe the idealized ground geometries for complexes with high coordination numbers i.e. the regular

of monodentate ligands. A general discussion of the established ground geometries and a number of suggested ground geometries for complexes with CN seven to twelve is given by Mutterties and Wright.⁵⁸ Separate analyses of the stereochemistry of eight-coordinate complexes are made by Lippard⁵⁹ and by Hoard and Silverton⁶⁰ and nine-coordinate complexes are discussed by Albertsson¹ and by Day and Hoard.⁶¹

It is evident from these compilations that the most probable idealized polyhedra for a nine-coordinate complex are the D_{3h} tricapped trigonal prism (TCTP) and the less symmetrical C_{4v} monocapped square antiprism (CSAP). These polyhedra are illustrated in Fig. 9 a and b. The numbering of the ligand atoms of the TCTP is made according to the rules recommended by IUPAC⁶² while the numbering in the CSAP is chosen in order to elucidate the close relationship between the two polyhedra. Only slight distortions are needed to convert the CSAP into a TCTP with the triangular faces 1, 2, 3 and 7, 8, 9.



(a)



(b)

Fig. 9. Probable idealized polyhedra for nine-coordinate complexes.
(a) tricapped trigonal prism, (b) monocapped square antiprism.

The most common ground polyhedra for eight-coordinate complexes are the D_{4d} square antiprism (SAP) and the D_{2d} dodecahedron (DOD). Another possible but less frequent polyhedron is the C_{2v} bicapped trigonal prism (BCTP), which is a hybrid between the DOD and the SAP. These three eight-coordinate polyhedra are shown in Fig. 10 a, b, and c. The numbering of the ligand atoms of the SAP follows the IUPAC rules but again the numbering of the other polyhedra is different from these rules and chosen in order to emphasize the relationship between the polyhedra. The DOD may be thought of as formed by two intersecting trapezoids perpendicular to each other. The trapezoid "arms" are indicated by bold lines in Fig. 10 b.

The energy difference between the described idealized ground geometries for each particular CN will not be large,^{58,61} and whether a given complex in the solid state comes close to one regular polyhedron or another is probably highly dependent on

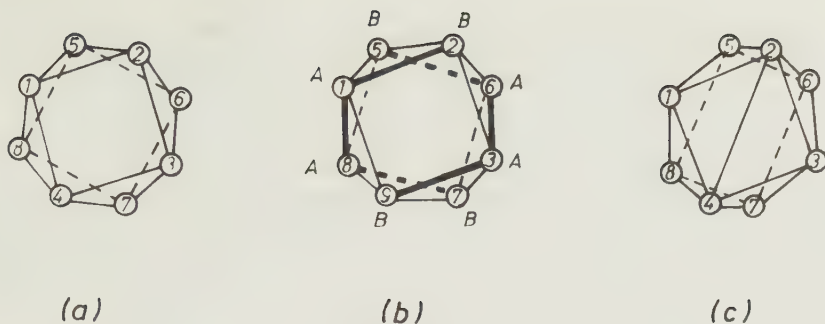


Fig. 10. Probable idealized polyhedra for eight-coordinate complexes. (a) square antiprism, (b) dodecahedron, (c) bicapped trigonal prism.

packing forces. The adoption of different coordination geometries for neodymium malonate complexes of identical composition in the structures of NDO and NDH is a good example of this fact (see below).

Real complexes are generally distorted from the regular ground polyhedra. Kepert⁶³ has calculated the distortions from the hard sphere models (HSM) of the SAP, DOD, and TCTP which are needed to minimize the ligand-ligand repulsions in a purely ionic complex with all ligands identical, monodentate and at the same distance from the central ion. Similar calculations for the SAP and DOD have been performed by Hoard and Silverton.⁶⁰ Since the results are of some interest for the following discussion a brief account may be appropriate.

It is assumed that the repulsive energy, u_{ij} , between any two

donor atoms i and j is given by $u_{ij} = u_C + u_B$, where u_C is the energy due to Coulombic repulsion and u_B is the energy due to Born-Mayer repulsion. The total repulsive energy U is equal to $\sum u_{ij}$ i.e. composed of a Coulombic term and a Born term. A regular polyhedron of given symmetry is defined by one or two geometrical parameters (see below). Kepert calculates the values of these parameters that result in a minimum for each particular energy term. The Born repulsive energy between two ligands is assumed to be proportional to d_{ij}^{-n} , where d_{ij} is the distance between the two ligands. The calculations are performed for $n = 6$ and $n = 12$.

A regular SAP is defined by the angle θ_{SAP} that the metal-ligand bonds form with the eight-fold inversion axis. The HSM-value of θ_{SAP} is 59.3° but a more favourable structure should be obtained if θ_{SAP} is lowered by $2-3^\circ$.

There are two different types of ligand positions in a dodecahedron. They are denoted by A and B in Fig. 10 b. The angles θ_A and θ_B that the M-A and M-B bonds make with the four-fold inversion axis respective, define a regular DOD. The minimum repulsive energy is obtained by increasing θ_B by about 2° from the HSM value, 69.5° .

Finally, a regular TCTP is defined by the ratio ρ between the equatorial and the prismatic metal-ligand bonds and the angle θ_{TP} that the prismatic metal-ligand bonds make with the three-fold axis. The HSM-value of θ_{TP} varies with ρ . In the region $0.8 \leq \rho \leq 1.1$ the variation is approximately linear and $37.0^\circ \leq \theta_{TP} \leq 43.6^\circ$. For these values of ρ a more stable structure will be obtained by increasing θ_{TP} by about 3° from the HSM-value.

The actual complexes do not fit very well to this model. The

metal-oxygen bonds are of different lengths varying with about ± 0.1 Å around the average value in each particular complex. The ligands are not identical, bidentate carboxylate ligands, water molecules, and carboxylate oxygens from adjacent complexes enter into the coordination sphere. Further, the water molecules and most of the carboxylate oxygens take part in hydrogen bonding. Even though large variations in bond distances and angles are possible both around hydrogen bonded water molecules⁶⁴ and around hydrogen bonded carboxylate groups⁶⁵, it must be assumed that the hydrogen bonding plays an important role in determining the detailed shape of the coordination polyhedron. This is indicated by the constancy of corresponding hydrogen bonded oxygen-oxygen distances in pairs of isostructural compounds as $M(\text{glycolate})_3$ $M = \text{La}$ and Gd ,⁴³ $\text{Na}_3M(\text{oxydiacetate})_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ $M = \text{Nd}$ and Yb ,¹¹ and YBOX and SCOX. In each of these structures the change in size of the central ion is accompanied by significant distortions of the coordination polyhedron while the hydrogen bond distances are almost unaffected. The observed changes are less than 0.01 Å for distances shorter than 2.8 Å and less than 0.06 Å for distances in the range 2.8 – 3.2 Å.

With this background it is not surprising to find that the coordination polyhedra of the investigated complexes are fairly distorted versions of the common ground geometries. In order to describe the distortions a number of distances and angles within the polyhedra are collected in Tables 6 and 7 and these data are for each complex compared to the HSM-value of the closest related regular polyhedron. The HSM-values have been calculated assuming all M-O bond lengths to be equal to the average M-O bond distance of the actual complex. The glycolate complexes investigated by Grenthe^{43-45,48} are included in these Tables to give a more complete picture of the coordination geometries adopted by

Table 6. The distortions of the coordination polyhedra of some nine coordinate lanthanoid carboxylate complexes from a regular tricapped trigonal prism. The ligand glycolate is abbreviated glyc.

Compound	Edge of prismatic triangle		Height of prism		Tilt angles			ρ		Θ_{TP}		M-O	
	range	average	range	average	V_{13}	V_{12}	V_{23}	range	average	range	average	range	average
NDOX	2.97-3.33	3.08	2.91	3.25-3.67	3.45	3.70	7 11 9	1.00-1.04	1.02	36-53	46	2.46-2.57	2.50
NDO	2.83-3.31	3.09	2.91	2.91-3.88	3.34	3.70	18 14 10	0.95-1.11	1.02	32-61	50	2.41-2.72	2.50
NDH	2.80-3.37	3.03	2.93	2.78-3.46	3.41	3.68	5 8 8	1.00-1.09	1.04	35-50	45	2.35-2.61	2.50
EUM	2.79-3.54	3.08	3.02	3.18-3.23	3.21	3.61	1 5 4	1.02-1.20	1.12	43-51	48	2.37-2.84	2.51
La(glyc) ₃	2.86-3.40	3.13	2.97	3.18-3.88	3.52	3.78	14 4 11	0.99-1.06	1.02	28-58	45	2.44-2.59	2.55
Gd(glyc) ₃	2.95-3.33	3.08	2.84	3.05-3.66	3.32	3.64	13 3 11	0.99-1.06	1.01	39-53	45	2.35-2.49	2.45
Eu(glyc) ₃	2.88-3.26	3.05	2.98	3.23-3.51	3.38	3.65	5 4 5	1.01-1.11	1.07	39-56	46	2.44-2.70	2.51

Table 7. The distortions of the coordination polyhedra of some eight-coordinate lanthanoid carboxylate complexes from a regular dodecahedron or square antiprism. The ligand glycolate is abbreviated glyc and oxacetate oac.

Compound	δ		Θ_A		Θ_B		Θ_{SAP}	
	range	HSM	range	average	range	average	range	average
YBOX	9-12	0	34.6-38.4	36.5	36.9	70.3-73.0	71.6	69.5
SCOX	12-17	0	36.5-37.4	36.9	36.9	71.2-73.4	72.5	69.5
EUM	28-25	24.5	—	—	—	54.5-59.5	57.5	59.3
Er(glyc)(oac) · 2H ₂ O	4-5	0	34.5-37.4	35.9	36.9	69.6-73.6	71.5	69.5
Er(glyc) ₃ · 2H ₂ O (I)	16	24.5	—	—	—	53.0-60.0	56.5	59.3
Er(glyc) ₃ · 2H ₂ O (II)	12-20	24.5	—	—	—	53.0-59.5	56.3	59.3

lanthanoid complexes formed with bidentate carboxylate ligands in the solid state. No additional structures of lanthanoid compounds with ligands of this type seem to be known.

In Table 6 all the nine-coordinate complexes are described as distorted TCTP:s. Some of the quantities listed may need some explanation. The tilt angle v_{13} is the angle between the triangular faces of the prism and v_{12} and v_{23} are the angles between each of these triangular faces and the equatorial plane i.e. the plane defined by the three capping oxygens. Since the triangular faces are non-parallel, the height of the prism is defined as the average distance of the atoms of one triangular face to the other triangular face. The parameters θ_{TP} and ρ have been defined above. In calculating θ_{TP} the normal to the equatorial plane was taken as the three-fold axis.

The largest deviations from the TCTP model are found for the NDO-polyhedron. As pointed out in Ref. 5, this polyhedron is better described as a CSAP. In a regular CSAP the angle between the triangular faces 1,2,3 and 7,8,9 (see Fig. 9) is 18° i.e. just the value found for v_{13} in NDO. The neodymium malonate complexes in NDO and NDH have identical compositions but are involved in different hydrogen bond systems. The CSAP model was used to describe the NDH polyhedron in order to facilitate the comparison of the two complexes but it was noted that the TCTP model might be a better description of this polyhedron. It is obvious from Table 6 that this is the case, and it can be concluded that the possibilities of hydrogen bond formation determine the type of coordination geometry adopted by this complex. This finding is in agreement with the statement made by Day and Hoard⁶¹ that the energy difference between the TCTP and CASP should be too small to give a definite criterion of stereochemical preference.

In all polyhedra but that of NDO the average value of θ_{TP} is $2-4^\circ$ larger than the HSM-value i.e. just the distortion predicted by Kepert. This increase in θ_{TP} is reflected in an increase in average edge length of the prismatic triangles and a decrease in height of the prism. The same agreement between Kepert's calculations and the experimental findings was obtained for the lanthanoid oxydiacetate and dipicolinate complexes ML_3^{3-} . The latter complexes are described in Table 5 in Ref. 1. A comparison of these data with those given in Table 6 reveals that the "bidentate" complexes are more severely distorted than the "tridentate" complexes, e.g. for the tridentate complexes the maximum range of θ_{TP} is 5° , the maximum range in triangular edge length is $0.13 \text{ \AA}$ and the largest tilt angle is 5° .

It may thus be concluded that the larger freedom at the formation of a coordination polyhedra possessed by a combination of bi- and monodentate ligands as compared to three tridentate ligands results in (i) a decrease in coordination number for the smallest lanthanoid ions and (ii) a higher degree of distortion from the TCTP model for the bidentate complexes than for the tridentate complexes. As just mentioned, the distortions in NDO result in a polyhedron best described as a CSAP, which is a highly improbable arrangement in a complex with three identical tridentate ligands.

The distortions of the eight-coordinate polyhedra are illustrated in Table 7. The values of θ_A and θ_B or of θ_{SAP} are compared with the HSM values. The various angles were defined above. These polyhedra are also fairly irregular and as a result of this it is sometimes hard to determine the best ground geometry for the description. This problem has been studied by Aslanov and Porai-Koshits.⁶⁶ They propose some criteria for determining the polyhedral shape. An easily applied rule is the following.

Describe the polyhedron with the "best" dodecahedron. Calculate for each of the trapezoids the angle between the plane that passes through the two A ligand sites and the midpoint of the line B-B, and the plane that passes through the two B positions and the midpoint of the line A-A (see Fig. 10). In a DOD this angle is 0° , in a BCTP it is 16.1° and in a SAP it is 24.5° .

This angle has been calculated for the polyhedra included in Table 7 and is denoted δ . It is seen that the polyhedra of EUM and $\text{Er}(\text{glyc})(\text{oac}) \cdot 2\text{H}_2\text{O}$ come close to a DOD and a SAP, respectively, while those of YBOX and SCOX are intermediate between a DOD and a BCTP. There are two different polyhedra in $\text{Er}(\text{glyc})_3 \cdot 2\text{H}_2\text{O}$ denoted I and II. Both polyhedra were described with the DOD model in Ref. 48. The values of δ indicate that I is a BCTP while II is intermediate between a BCTP and a SAP.

If the SAP description is used for the two $\text{Er}(\text{glyc})_3 \cdot 2\text{H}_2\text{O}$ polyhedra and EUM and the DOD description for the other polyhedra, the distortions from the HSM models are found to be close to those predicted by Kepert in all cases. It is interesting to note that when the DOD model was used for the $\text{Er}(\text{glyc})_3 \cdot 2\text{H}_2\text{O}$ polyhedra the average values of θ_A and θ_B were about 38° and 76° , respectively, i.e. far from those predicted by Kepert. It is obviously important to choose the best description of the polyhedron for the comparison of experimental and theoretically calculated values of θ .

THE OXALATE IONS

Each oxalate ion in the compounds $\text{M}_2\text{ox}_3 \cdot n\text{H}_2\text{O}$, $n = 6$ or 10 , is planar, possesses a center of symmetry, and is bridging between two metal ions forming two identical five-membered chelate rings.

The two metal ions are in each case less than 0.2 Å out of the plane of the oxalate ion. The dimensions of the ligands are in all cases compatible with those found in other oxalate structures.

No significant influence on the ligand geometry attributable to the change in size of the central ion was found. The decrease in ionic radius involved is 0.26 Å between Nd(III) in nine-coordination ($r = 1.13$ Å) and Sc(III) in eight-coordination ($r = 0.87$ Å). The ionic radii used here and in the following discussion are for $CN \leq 8$ taken from Shannon and Prewitt.¹³ The radii of the nine-coordinate rare earth ions are assumed to be 0.13 Å larger than the corresponding radii for $CN = 6$. This relationship has been proposed by Albertsson.¹ The radii in nine-coordination thus obtained are almost identical with those in eight-coordination since the differences $r_{CN=8} - r_{CN=6}$ range from 0.11 Å to 0.14 Å within the lanthanoid series.

A considerable number of structures of metal oxalate complexes are known. Interatomic distances and angles of the oxalate ions in the thirteen different complexes whose structures have been determined from three-dimensional X-ray intensity data, are collected in Table 8. This has been made in order to get some idea of the extent to which the dimensions of the oxalate ion may be affected by changes in the central ion.

In eight of the compounds the oxalate ions are non-bridging, *i.e.* chelated only to one metal ion. The non-chelating oxygens in these structures are hydrogen bonded or coordinated to alkali metal ions. Five compounds contain bridging oxalate ions of the type found in the rare earths oxalates. The alkali oxalates $K_2ox \cdot 2H_2O$ ⁶⁷ and Li_2ox ⁶⁸ are included in Table 8. The metal-ligand interactions are expected to be weaker in these compounds than in the metal complexes, and the oxalate ions of the alkali

Table 8. Survey over dimensions of the oxalate ion in complexes with various metal ions.

Compound	Bond distances (Å)						Bond angles (°)						Ref.	Notation	
	C1-O1	C2-O3	C1-O2	C2-O4	C1-C2	O1-O3	O2-O4	C-C-O1	C-C-O3	C-C-O2	C-C-O4				
$K_2\alpha\cdot H_2O$	1.260	1.247	1.247	1.260	1.574	2.707	2.707	115.7	118.0	118.0	115.7	126.3	126.3	67	
$Li_2\alpha$	1.257	1.247	1.247	1.257	1.559	2.675	2.675	116.3	116.4	116.4	116.3	127.3	127.3	68	
$H_2\alpha\cdot 2H_2O$	1.285	1.212	1.212	1.285	1.538	2.635	2.635	112.1	121.1	121.1	112.1	126.8	126.8	69	
Non-bridging $KClOx_2\cdot 5H_2O$	1.271	1.232	1.202	1.203	1.569	2.584	2.782	114.3	112.3	118.9	121.7	126.8	126.0	70	
$Na_4ZrOx_4\cdot 3H_2O$	1.281	1.271	1.222	1.222	1.545	2.563	2.778	112.7	114.1	121.8	118.7	125.5	127.2	60	
$(NH_4)_3Nb(Ox)_2\cdot H_2O$	1.284	1.286	1.225	1.217	1.551	2.59	-	114.0	113.6	119.9	121.3	125.2	125.2	71	
$(NH_4)_3NbOx_3\cdot H_2O$	1.28	1.29	1.23	1.20	1.54	2.51	-	113	111	121	121	126	128	72	
$BoMo_2O_4Ox_2\cdot 5H_2O$	1.27	1.25	1.17	1.20	1.61	2.57	-	112	113	120	117	129	130	74	
$K_2Mo_2O_3Ox_2\cdot 2H_2O$	1.30	1.27	1.21	1.26	1.52	2.63	2.76	115	116	120	120	125	124	75	
$K_2PtOx_2\cdot 4H_2O$	1.29	1.29	1.21	1.23	1.54	2.65	2.79	115	116	121	120	124	124	76	
Average	1.28	1.22	1.22	1.22	1.59	2.59	2.59	114	114	121	121	126	126		
Range	1.25 - 1.30	1.17 - 1.23	1.17 - 1.23	1.17 - 1.23	1.25 - 2.65	2.51 - 2.80	2.51 - 2.80	110 - 116	110 - 116	116 - 123	116 - 123	124 - 132	124 - 132		
Bridging															
$SCOX$	1.244	1.265	1.265	1.244	1.537	2.648	2.648	115.2	117.3	117.3	115.2	127.5	127.5	3	
$NH_4\cdot V\cdot Ox_2\cdot H_2O$	1.27	1.26	1.26	1.27	1.47	2.65	2.65	117	118	118	117	124	124	2	
$NDOX$	1.22	1.28	1.28	1.22	1.56	2.67	2.67	115	116	116	116	129	129	77	
$YBOX$	1.29	1.28	1.28	1.29	1.59	2.73	2.73	117	115	115	117	127	127	4	
$UO_2Ox\cdot 3H_2O$	1.36	1.27	1.27	1.36	1.48	2.80	2.80	119	123	123	119	130	130	78	
Average	1.26	1.26	1.26	1.26	1.55	2.66	2.66	117	117	117	117	126	126		
Range	1.15 - 1.36	1.15 - 1.36	1.15 - 1.36	1.15 - 1.36	1.47 - 1.59	2.51 - 2.80	2.51 - 2.80	108 - 123	108 - 123	116 - 123	116 - 123	124 - 132	124 - 132		

oxalates might be compatible with a "free" oxalate ion. The dimensions of the $(\text{COO})_2$ group of $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ ⁶⁹ are also given to illustrate an oxalate group with C-O bonds of different character.

All the oxalate ions involved are approximately planar. The largest deviation from planarity is reported for $\text{K}_2\text{Pto}_2 \cdot 2\text{H}_2\text{O}$ ⁷⁶, where the two COO -planes are twisted by 3.4° , with respect to each other, around the C-C bond.

Considering the non-bridging oxalate ions the oxygens are of two different types, which may be described as chelating, O_C , and non-chelating, O_N . Judging from the data of Table 8 the bonds $\text{C}-\text{O}_\text{C}$ tend to be longer than the bonds $\text{C}-\text{O}_\text{N}$ and the angles $\text{C}-\text{C}-\text{O}_\text{C}$ are commonly smaller than the angles $\text{C}-\text{C}-\text{O}_\text{N}$. The averages of these quantities are compatible with those of the different C-O bonds and C-C-O angles in H_2ox .

There is no difference in the bonding situation of the four oxygens of a bridging oxalate ion, apart from the fact that some of the oxygens may accept a weak hydrogen bond from a water molecule. Accordingly, there is no reason for dividing the C-O bonds and C-C-O angles into two groups. The variation in C-O bond length and C-C-O angles is commonly less than was found in the non-bridging oxalate ions and the dimensions of the bridging oxalate ions are close to those of the hypothetical "free" ion. The oxalate ion of $\text{UO}_2\text{ox} \cdot 3\text{H}_2\text{O}$ ⁷⁸ is an exception and exhibits the combination of bond distances and angles characteristic of the $(\text{COO})_2$ group of H_2ox .

The average bite of the non-bridging oxalate ions, $2.59 \text{ \AA}$, is less than for the "free" oxalate ion while the average bite of the bridging oxalate ions, $2.66 \text{ \AA}$, is compatible with the "free" ion

Table 9. The ligand bite of the oxalate ions and some properties of the metal ions in oxalate complexes. The quantities given are defined in the text.

Compound	M - O _x (Å) x	CN	r (Å)	average bite (Å)
KCr ox ₂ · 5 H ₂ O	1.96	6	0.62	2.58
K ₂ Pd ox ₂ · 4 H ₂ O	2.00	4	0.64	2.63
K ₂ Pt ox ₂ · 2 H ₂ O	2.00	4	-	2.65
BaMo ₂ O ₄ ox ₂ · 5 H ₂ O	2.13	6	0.63	2.59
(NH ₄) ₃ NbO ox ₃ · H ₂ O	2.13	8	-	2.55
(NH ₄) ₃ Nb(O ₂) ₂ ox ₂ · H ₂ O	2.14	7	0.66	2.59
K ₂ Mo ₂ O ₅ ox ₂ · 2 H ₂ O	2.14	6	0.60	2.57
Na ₄ Zr ox ₄ · 3 H ₂ O	2.20	8	0.84	2.57
SCOX·	2.23	8	0.87	2.64
YBOX	2.34	8	0.98	2.71
NH ₄ Y ox ₂ · H ₂ O	2.40	9	1.02	2.68
UO ₂ ox · 3 H ₂ O	2.49	7	0.88	2.53
NDOX	2.51	9	1.13	2.66

value. The ranges of bite in the two groups overlap, however, and the dividing of the oxalate ions into bridging and non-bridging may be artificial in this respect.

In an attempt to relate the ligand bite to some property of the central ion, the metal ionic radius, r , and the average bond distance, $M - O_x$, between the metal ion and the oxalate oxygens are given in Table 9. There is no obvious correlation between r or $M - O_x$ and the ligand bite. However, not only the size but also the charge of the metal ion must be taken into account. One way to do this has been proposed by Lingafelter and Brown.⁷⁹ They studied the variation in ligand bite of the acetylacetonate ion (acac) when coordinated to different metal ions, and found an approximately linear relationship between the bite and the

ratio r/Q , where Q is the formal charge of the metal ion. The Pauling crystal radii⁸⁰ were used and the correlation coefficient was 0.81. However, it does not seem very reasonable to use the quantity r/Q for transition elements whose metal-oxygen bonds are fairly different in character. As a matter of fact when the five lanthanoid acetylacetonates (see Table 5) are added to the data of Lingafelter and Brown, and the radii for the actual coordination numbers¹³ are used instead of the Pauling radii (for CN 6), the correlation coefficient between the bite of acac and r/Q is reduced to 0.22.

There seems to be no simple relationship between ligand bite and the properties of the metal ion. In spite of this, the rare earth complexes with similar bonds between the central ion and the ligands should exhibit a slight decrease in bite with decreasing size of the central ion, but for all ligands so far investigated this effect is less than the estimated standard deviations.^{1,43}

THE MALONATE IONS

The knowledge of the structure of the malonate ion when coordinated to a metal ion, besides that obtained in the present work is limited to a preliminary report of the structures of the complexes Co(malonate)_2 (ethylenediamin)⁻ and $\text{Cr(malonate)}_3^{3-}$.⁸¹ No atomic coordinates or interatomic distances and angles are included in that paper but some information of the conformation of the six-membered chelate ring is given. The various malonate ions in the rare earth malonates are compared to each other and to the malonate residues of potassium hydrogen malonate, KHmal ,⁸² and malonic acid⁸³ in Table 10. The structure of KHmal is accurately determined while that of malonic acid is more approximate as it is based upon incomplete data.

Table 10. The conformation of the malonate ion and of the six-membered chelate ring. The quantities given are defined in the text. Abbreviations of organic ligands: mal: malonate, en: ethylenediamine, pn: 1,2-diaminopropane.

Compound	V_1 ($^\circ$)	V_2 ($^\circ$)	C-C-C ($^\circ$)	O-O ($\text{\AA}$)	d_M ($\text{\AA}$)	d_C ($\text{\AA}$)
KHmal	5	-5	119.4	2.80	-	-
H ₂ mal	≈ 0	≈ 90	110	-	-	-
<u>nonchelating</u>						
NDO	50	-50	113(2)	3.24(2)	-	-
NDH	70	-70	104(2)	3.42(2)	-	-
<u>chelating</u>						
NDO	40	48	117(1)	2.83(2)	0.42	0.50
NDH	32	44	118(1)	2.80(2)	0.33	0.43
SCM	35	41	115(1)	2.74(1)	0.32	0.45
EUM	45	45	115(4)	2.79(4)	0.51	0.31
EUM	28	28	112(3)	2.84(4)	0.29	0.67
EUM	55	55	115(5)	2.89(5)	0.60	-0.45
Co(pn) ₃ Cr(mal) ₃	-	-	-	-	0.00	0.69
NaCo(mal) ₂ en	-	-	-	-	0.42	0.45
NaCo(mal) ₂ en	-	-	-	-	0.61	0.36

The malonate ions in the rare earth malonates are of two different types, those forming a six-membered chelate ring and those which do not form such rings. For both types of ions the bond distances and angles are compatible with those found in KHmal and malonic acid, except for the C-C-O angles, which within each of the latter structures differ with about 10° as a result of the different nature of the C-O bonds. In all cases the C-COO groups are planar within the limits of errors.

The conformation of the chelating malonate ions is completely different from that of the non-chelating ions. The conformation of a malonate ion with planar C-COO groups may be described by the angles between the planes of each of these groups and the carbon chain plane. These angles are denoted v_1 and v_2 and are given in Table 10. The two angles have the same sign when both carboxylate groups are twisted in the same direction out of the carbon chain plane and opposite signs when the twists are in opposite directions.

Two non-chelating malonate ions are represented in the structures studied. In both ions the methylene carbon is situated on a two-fold axis and thus the carboxylate groups are twisted in opposite directions. The twists are 50° and 70° , respectively, and result in almost maximum separation of the oxygens belonging to different COO groups (O-O in Table 10). A similar conformation might be expected for a hypothetical "free" malonate ion since it would result in minimum O-O repulsion.

The chelating malonate ions adopt a conformation where the two COO groups are twisted in the same direction out of the carbon chain plane by about 45° . In this conformation the shortest separation of two oxygens not belonging to the same COO group is about 2.80 Å. This distance, the ligand bite, does not vary significantly between the structures.

Included in Table 10 are the C-C-C bond angles in order to illustrate that they, for the chelating malonate ions, are invariably larger than the tetrahedral value. The same feature is found in the almost planar malonate residue of KHmal. This large C-C-C angle together with the large C-C-O angle (124.4°) results in a O-O separation of 2.80 Å in KHmal. With "normal" bond angles (i.e. 109 and 117° , respectively) the O-O separation of a completely planar malonate ion would be less than 2.5 Å.

The conformations of the nine six-membered malonate chelate rings, whose structures are known, are given in Table 10. In all these rings the four carboxylate atoms are approximately coplanar. The distances of the metal ion and the methylene carbon to this plane are denoted d_M and d_C , respectively. Seven of the rings adopt a boat conformation with the metal ion and methylene carbon about 0.5 Å out of the central plane in the same direction. One ring has a chair conformation, with the

metal ion and methylene carbon at different sides of the plane and one ring may be described as a boat flattened at one end since the metal ion is approximately in the central plane while the methylene carbon is out of that plane.

This limited material thus indicates that the preferred conformation of a chelating malonate ion may be that with the two COO-groups twisted by 45° in the same direction out of the carbon chain plane and that the six-membered chelate ring preferentially adopts a boat conformation.

THE WATER MOLECULES

The bonding situation of water molecules in crystal hydrates has been extensively studied. A classification of the hydrate water molecules based on the coordination of the lone pair orbitals was first proposed by Chidambaram et al.⁸⁴ It has been slightly modified by Hamilton and Ibers⁸⁵ and further revised by Ferraris and Franchini-Angela.⁶⁴ The latter work is based on about 40 hydrate structures investigated by neutron diffraction i.e. structures where the hydrogen positions are unequivocally established.

The notation used in the classification is shown in Fig. 11. A1 and A2 are the acceptors of the hydrogen bonds from the water molecule with the oxygen atom W. Water molecules with non-hydrogen bonded protons seem to be rare and are not covered by the classification. B1, B2, and B3 are cations that contact the water molecule at the lone-pair side. The water molecules are divided into four classes according to the number of cation contacts. Each class is further divided into different types on the basis of the chemical nature of the contacting cations, as shown in Table 11.

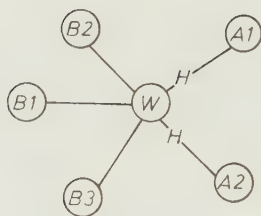


Fig. 11. The notation used in the classification of hydrate water molecules according to Ferraris and Franchini-Angela.

Water molecules belonging to class 1 and 1' are contacted by one cation, B1. The W-B1 bond is directed along the bisector of the lone pair orbitals in class 1 and along a lone pair orbital in class 1'. In class 2 there is one cation along each of the lone pair orbitals of the water molecule, resulting in an approximately tetrahedral arrangement around W. Three cations contact W in class 3. B1 is approximately in the plane of the water molecule and B2 and B3 are perpendicular to that plane in such a way that the polyhedron around W is essentially a trigonal bipyramid. Water molecules for which no specific cation interaction is discernible are assigned to class 4.

The classes 1 and 1' do not appear to be very well-defined. For the water molecules that according to Ferraris and Franchini-Angela belong to class 1 the H-W-B1 angles range from 110 to 140° and for water molecules belonging to class 1' they range from 103 to 122°. It is hard to see the difference between a class 1 water molecule with H-W-B1 angles 116 and 124° and a class 1' water molecule with the corresponding angles 115 and 122°. Considering the rather undirected character of the W-B bonds, it seems

Table 11. Classification of water molecules in crystal hydrates according to Ferraris and Franchini-Angela.

	Type	B 1	B 2	B 3
Class 1	C	M^+	-	-
	D	M^{2+}	-	-
	F	H^+	-	-
	M	M^{n+}	-	-
Class 1'	I	M^+	-	-
	J	M^{2+}	-	-
	K	H^+	-	-
	N	M^{n+}	-	-
Class 2	A	-	M^+	M^+
	B	-	M^{2+}	M^{2+}
	E	-	H^+	H^+
	G	-	M^+	H^+
	H	-	M^{2+}	H^+
Class 3	O	M^+	M^+	M^+
	P	H^+	M^+	M^+
	Q	M^+	M^+	H^+
	R	M^+	H^+	H^+
	S	H^+	H^+	M^+
	T	H^+	H^+	H^+

more reasonable to describe water molecules in crystal hydrates by the number and nature of the cation contacts, without emphasizing the directions of the bonds. For water molecules whose exact hydrogen atom positions are not known it is necessary to confine the description in this way.

In structures where only the heavy atoms have been located the hydrogen bond situation may often be predicted by geometrical considerations as described in detail by Baur.⁸⁶ Probable hydrogen bonds of most of the water molecules involved in the rare earth oxalates and malonates covered by the present investigation have been determined from the following criteria. Oxygens within

Table 12. Classification of the water molecules in rare earth oxalates and malonates.

Compound	Water oxygen	B 1	B 2	B 3	A 1	A 2	Class	Bond-angles
YBOX, SCOX	O(7)	M ³⁺	-	-	OC	OC	1 MN	351
	O(9)	M ³⁺	-	-	OC	OH ₂	1 MN	340
NDO	O(7)	-	M ³⁺	H ⁺	OC	OC	2 U	95-133
	O(8)	M ³⁺	-	-	OC	OH ₂	1 MN	341
	O(9)	M ³⁺	-	-	OC	OH ₂	1 MN	335
	O(10)	-	H ⁺	H ⁺	OH ₂	OC	2 E	59-159
NDH	O(7)	M ³⁺	-	-	OC	OC	1 MN	357
	O(8)	M ³⁺	-	-	OC	OH ₂	1 MN	359
	O(9)	M ³⁺	-	-	OC	OC	1 MN	341
EUM	O(W1)	M ³⁺	-	-	OC	OC	1 MN	355
	O(W2)	M ³⁺	-	-	OH ₂	OH ₂	1 MN	355
	O(W3)	M ³⁺	-	-	OC	OC	1 MN	355
	O(W4)	M ³⁺	-	-	OH ₂	OH ₂	1 MN	344
	O(W5)	M ³⁺	-	-	OC	OC	1 MN	330
	O(W6)	-	H ⁺	H ⁺	OC	OC	2 E	83-138
SCM	O(6)	M ³⁺	-	-	OC	OH ₂	1 MN	357
	O(7)	H ⁺	-	-	OC	OC	1 FK	342

3.20 Å from the actual water oxygen are assumed to be possible hydrogen bond acceptors. For water molecules coordinated to a metal ion, other oxygens coordinated to the same metal ion are excluded as acceptors since hydrogen bonds along edges of a coordination polyhedron around a trivalent metal ion are highly improbable on energetic grounds. According to Baur a hydrogen bond of this type has never been established.^{86,87}

Among the 24 water molecules involved, 17 were found to have only two probable acceptors. Their bonding situation is described in Table 12. The acceptors A1 and A2 are carboxylate oxygens (OC) or water oxygens (OH₂). The "bond" angles included in Table 12 are for class 1 water molecules the sum of the heavy-atom neighbour angles around W and for class 2 water molecules the range of these bond angles.

Only one water molecule coordinated to M^{3+} belongs to class 2, viz. O(7) in NDO. This type of water molecule making cation contacts to M^{3+} and H^+ is not covered by Ferraris' classification and is denoted 2 U in Table 12. Class 1 and class 2 water molecules seem to be equally frequent among crystal hydrates as far as mono and bivalent metals ions are involved. In the rare earth hydrate structures listed in Table 5 and in Ref. 1, Table 6 the water molecules coordinated to M^{3+} invariably belong to class 1. Thus the dominance of class 1 water molecules found in the present investigation seems to be general for rare earth hydrates.

When more than two possible acceptors are found at approximately the same W-O distance the hydrogen bonds can not be predicted with any certainty by geometrical considerations. Further the possible existence of bifurcated hydrogen bonds must be taken into account. This situation was found for the water oxygen O(8) in SCOX and YBOX. One of the possible acceptors for the protons of this water molecule is the centrosymmetric equivalent of O(8), cf. O(8ⁱⁱⁱ) and O(8^{vii}) in Fig. 2. A similar situation was found for O(8) in NDH, and has also been noted in a number of other crystal hydrates.^{88,55,56} The interpretation of such distances as hydrogen bonds implies either the absence of the centre of symmetry insofar as the protons are concerned or else some disorder in the proton arrangement.

The approximate hydrogen positions in SCOX have been located in a reinvestigation of the structure based on single crystal X-ray diffractometry data. This investigation indicates that a hydrogen bond interaction O(8ⁱⁱⁱ)-O(8^{vii}) exists and that the hydrogen atoms of the two water molecules are not centrosymmetrically related. One proton of O(8^{vii}) is bonded to O(8ⁱⁱⁱ) while the other is bonded to O(6^{vii}). The protons of O(8ⁱⁱⁱ) interact weakly with O(2ⁱⁱⁱ) and

O(7^v), respectively. According to these results the water molecule O(7) classified as 1 MN in Table 12 should belong to class 2 U.

Some details of this reinvestigation of SCOX are given in Appendix II.

The water molecules of NDOX could not be classified since the structure contains a number of disordered water molecules that may take part in the hydrogen bond system. There are three water molecules with fixed positions, viz. those coordinated to Nd³⁺ (O(7), O(8), and O(9), see Fig. 1). They each have a carboxylate oxygen as one possible hydrogen bond acceptor while the other hydrogen atom is assumed to interact with the disordered water molecules. At room temperature the positions of these water molecules could not be detected in the electron density maps, but at -50°C several positions were found located in the "empty spaces" left by the packing of the neodymium oxalate layers. Most of these positions are within hydrogen bond distance from the coordinated water molecules. EUM also contains disordered water but in that structure probable hydrogen bond acceptors for the definitely located water molecules were found within the ordered parts of the structure.

It is often necessary to assume that a structure contains disordered water molecules located in cavities between the main structural elements. The principal role played by such disordered water is probably that of filling space. Since the tendency of water molecules to form hydrogen bonds is strong, it must, however, be assumed that these included water molecules are involved in hydrogen bonding to the surrounding oxygens and to each other. Sometimes, electron density interpretable as water oxygens with high temperature factors (10-25 Å²) is found in the actual space. Temperature factors of this magnitude indicate that the water

molecules are disordered around the average position obtained in the refinement. Such average positions are often found to be within hydrogen bond distance from each other indicating that the disordered water molecules may be bonded in pairs (e.g. in EUM¹⁹ and in $(\text{NH}_4)_3\text{Nb}(\text{O}_2)(\text{C}_2\text{O}_4)\text{H}_2\text{O}$ ⁷¹) or in short chains (e.g. in thymine monohydrate⁸⁹ and in caffeine hydrate⁹⁰). The low temperature study of NDOX indicates that the disordered water molecules also in that structure may be linked in pairs and short chains.

Because of the low accuracy in the determination of NDOX a meaningful comparison of the ordered parts of the structure between room temperature and -50°C was not possible. Thus the possible influence of the reduced mobility of the water molecules on these parts of the structure could not be studied. Higher accuracy might be obtained in a corresponding investigation of a structure with metal ions of lower atomic number. The compounds $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 18\text{H}_2\text{O}$ seem to be suitable objects. They probably contain metal oxalate networks similar to those of NDOX and SCOX and the high hydration numbers indicate the presence of several uncoordinated water molecules. It is also rather tempting to determine the structures of these or other compounds with high hydration numbers in order to study the possibilities of uncoordinated water molecules to form hydrogen bonded aggregates.

CONCLUSION

The original aim of the present investigation was to get information about rare earth complexes that might be useful in the interpretation of the results of thermodynamic studies of these complexes in solution. It seems appropriate to conclude by summarizing those

findings that may be of interest in this respect. However, it must be pointed out once again that results obtained in the solid state are not directly applicable to complexes in solution.

The conformation of the chelated malonate ion is found to be almost independent of the coordinated rare earth ion and of the crystallographic surroundings of the complex. This indicates that the conformation adopted in the solid state may be preferred also in solution and thus that the ligand bite is about 2.80 Å. The dimensions of the oxalate ion are also found to be approximately constant between the different rare earth structures, with a ligand bite of about 2.65 Å. Hence the fact that while a maximum of four oxalate ions are coordinated to the rare earths the corresponding number of malonate ions is three is probably not due to differences in ligand bite between the two ions.

Another result of interest concerning the malonate complexes is the finding of non-chelated malonate ions. This is in accordance with the proposed weak chelating tendency of the malonate ion observed in solution.

Of more general interest for the discussion of complex formation in solution is perhaps the changes in coordination number, observed both for the oxalates and the malonates, when going through the lanthanoid series. Whether a lanthanoid complex in the solid state is nine- or eight-coordinate is probably highly dependent on the possibilities of incorporating it into a favourable system of hydrogen bonds and/or carboxylate bridges. For example, the ligands glycolate and oxalate which from a geometrical point of view are very similar with bites of about 2.6 Å form complexes ML_4 with different coordination numbers with the smaller lanthanoids. The glycolates are eight-coordinate (in $M(\text{glyc})_3 \cdot 2H_2O$ ⁴⁸) while the oxalates are nine-coordinate (in $NH_4 \cdot M \cdot ox_2 \cdot H_2O$ ⁷⁷ and $H \cdot M \cdot ox_2 \cdot 3H_2O$ ⁹¹). Besides these two oxalate complexes

there are two other examples of hydrated complexes with chelating ligands that are nine-coordinate at the end of the lanthanoid series viz. in $M(\text{imin})(\text{H}_2\text{O})_3 \cdot \text{Cl}^{46}$ and in EUM. In both complexes bridging-chelating carboxylate groups belong to the coordination sphere resulting in one respective two M-O bond distances considerably longer than the average value indicating a coordination number intermediate between nine and eight. Further studies of the structures of hydrated lanthanoid chelates are needed to reveal whether a change in coordination number when going through the series is general or not. If it is found to be general it would strongly support the interpretation of thermodynamic data of complexation in solution in terms of changes in hydration number.

ACKNOWLEDGEMENTS

The present study was initiated by Dr. I. Grenthe. Dr. J. Albertsson introduced me into the field of X-ray crystallography. I wish to express my sincere appreciation to them for all encouragement, support and invaluable help during this research.

I also wish to express my appreciation to Prof. I. Leden for positive criticism and valuable discussions and to Prof. S. Fronæus for his kind interest in this project.

I should like to thank my colleagues for their friendly collaboration and particularly Drs. K. Aurivillius and Å. Oskarsson for valuable help and stimulating discussions, and Drs. C. Svensson and C. Sörnstrand for much help and advice during the computer work.

For technical assistance I wish particularly to thank Mrs. K. Andersson, Mrs. G. Jacobsson, Mrs. K. Johansson, Mrs. I. Mellqvist, Mrs. M. Molund, Mr. O. Hansson, Mr. H. Karlsson, and Mr. S. Jönsson. The English text has been revised by Dr. P. Sellers and his valuable help is much appreciated.

This investigation has been supported financially by the Swedish Natural Science Council. This is gratefully acknowledged.

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APPENDIX

I. The powder patterns of the rare earth oxalates and the observed and calculated structure factors of YBOX.

Table 1. Observed and calculated values of $10^4 \cdot \sin^2 \theta$ for the compounds $M_2(C_2O_4)_3 \cdot nH_2O$. A. The monoclinic decahydrates. The visually estimated powder intensities of the neodymium compound are included.

h k l	Ce		Nd		Sm		Gd		Dy		Ho		Er		I _{obs} Nd
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	
1 0 0	56	56	56	57	58	58	58	58	59	59	59	60	60	60	■
1 1 0	120	120	120	121	121	122	122	122	123	123	124	124	124	124	■
-1 1 0	150	151	151	152	152	153	154	154	156	156	156	156	157	157	■
0 1 1	156	156	156	157	158	159	160	160	162	162	162	162	163	163	■
-1 0 2	220	220	225	226	230	230	233	235	239	239	240	241	241	241	■
2 0 0	225	225	227	228	231	231	234	238	257	257	259	258	260	260	■
-2 1 1	257	257	259	260	263	263	266	268	286	286	286	286	286	286	■
0 2 0	257	257	255	255	255	256	256	256	257	257	257	258	257	257	■
1 1 1	255	254	255	257	260	260	263	266	266	266	268	268	268	268	■
-2 0 2	265	265	267	267	276	277	281	281	286	286	286	286	286	286	■
2 1 0	289	289	291	291	294	295	298	298	300	301	300	303	303	304	■
1 2 0	311	313	312	312	313	314	314	315	315	316	318	317	316	317	■
-1 2 1	322	323	323	323	325	325	327	328	329	329	329	330	329	329	vw
0 2 1	328	328	328	329	330	331	332	332	335	335	335	336	334	335	vw
0 1 2	351	352	352	354	363	364	369	369	374	374	377	377	374	375	■
-3 0 2	422	423	451	451	459	459	446	444	452	452	457	455	457	457	■
1 0 2	466	467	478	476	486	485	493	492	500	502	505	504	504	504	■
-1 2 2	476	477	481	481	486	486	493	492	500	502	505	504	504	504	■
-3 1 2	487	494	494	503	503	508	509	516	516	516	519	522	522	522	vw
3 0 0	504	506	513	512	519	520	526	525	534	533	537	536	539	539	■
0 2 2	543	544	549	549	555	555	560	561	568	567	569	570	570	570	■
2 2 2	570	570	576	576	584	584	587	588	590	596	597	601	601	601	■
-2 1 3	565	566	577	577	587	588	598	609	608	610	611	612	612	614	■
-1 1 3	582	582	594	594	605	606	615	615	627	626	629	629	632	631	■
1 3 0	633	634	631	631	635	635	638	638	649	649	650	651	651	651	■
-1 1 3	644	644	643	642	644	644	647	647	649	650	653	652	651	651	vw
-3 1 1	649	649	653	653	659	660	664	665	671	672	675	675	678	677	■
-3 2 1	661	661	674	674	686	687	695	697	709	708	712	712	716	715	■
-4 0 2	692	692	704	704	717	716	724	724	735	735	740	740	745	745	■
0 1 3	711	711	725	725	737	738	749	750	764	762	767	767	775	775	■
1 2 2	724	724	731	731	740	740	758	757	768	767	775	775	781	781	■
-2 1 2	751	750	750	750	755	754	758	758	768	767	775	775	781	781	■
3 2 0	752	752	767	767	777	776	783	782	789	790	793	794	796	796	■
2 0 2	760	759	771	766	785	796	795	804	807	812	815	816	815	815	■
-4 1 1	788	788	797	797	809	810	817	817	828	828	833	833	836	836	■
2 1 0	801	802	807	807	810	810	816	815	816	815	818	818	818	818	■
3 1 1	828	827	837	837	849	850	859	859	871	870	876	875	878	879	■
0 3 2	865	865	868	874	875	883	881	888	887	892	892	892	892	891	■
-3 2 3	852	855	866	878	878	889	901	901	906	906	906	906	906	906	■
-4 1 3	869	885	885	899	901	912	926	927	935	935	935	937	937	937	vw
-2 0 4	881	902	903	922	922	931	941	941	955	955	960	960	965	965	■
0 2 3	905	904	918	916	931	930	942	942	955	955	960	960	965	965	■
-3 0 4	917	915	917	937	957	973	991	991	996	997	1001	1000	1000	1000	vw
-4 2 2	947	949	959	959	971	972	982	981	995	995	998	998	1002	1002	vw
-1 0 4	960	960	981	982	1001	1001	1022	1020	1039	1039	1046	1046	1048	1048	■
-4 2 1	980	980	989	1002	1001	1001	1009	1009	1021	1021	1027	1030	1030	1030	■
-3 1 2	999	1000	1005	1005	1014	1014	1022	1021	1030	1030	1034	1034	1036	1036	■
2 2 2	1015	1016	1027	1027	1040	1041	1052	1052	1064	1070	1070	1070	1072	1075	vw
-4 2 3	1061	1076	1076	1093	1092	1104	1105	1120	1120	1126	1126	1128	1130	1130	■
-4 0 4	1043	1045	1095	1094	1098	1098	1101	1106	1106	1109	1108	1107	1107	1107	■
-1 3 3	1098	1098	1104	1104	1118	1117	1128	1141	1140	1145	1145	1145	1145	1145	■
3 2 2	1158	1158	1154	1154	1174	1174	1185	1185	1204	1202	1210	1210	1216	1217	■
-2 2 4	1119	1118	1158	1158	1178	1177	1196	1194	1211	1211	1218	1220	1222	1222	■
1 2 3	1145	1145	1161	1161	1178	1179	1196	1195	1211	1209	1218	1216	1216	1218	■
-4 1 4	1179	1174	1185	1184	1199	1198	1210	1209	1222	1222	1229	1228	1230	1229	■
-2 2 4	1172	1174	1192	1192	1214	1212	1231	1229	1247	1248	1255	1255	1259	1258	■
-2 4 1	1198	1194	1197	1199	1202	1202	1206	1211	1212	1212	1216	1216	1216	1215	■
-5 1 3	1189	1210	1209	1210	1210	1210	1245	1245	1264	1264	1272	1272	1281	1279	vw
0 1 3	1225	1225	1235	1250	1262	1262	1276	1284	1282	1282	1282	1282	1282	1282	■
-2 4 2	1247	1247	1247	1254	1262	1262	1267	1267	1276	1276	1276	1276	1276	1276	■
2 4 0	1249	1251	1248	1248	1254	1254	1260	1260	1267	1265	1270	1269	1270	1268	■
-5 1 1	1231	1231	1247	1247	1262	1267	1279	1278	1297	1295	1303	1304	1310	1311	■
1 1 1	1283	1282	1297	1297	1318	1318	1332	1331	1347	1349	1359	1358	1364	1364	■
2 1 3	1308	1307	1327	1327	1354	1351	1371	1369	1389	1391	1400	1399	1404	1402	■
-4 0 4	1322	1319	1347	1347	1375	1373	1393	1393	1416	1416	1427	1426	1434	1435	■
3 1 1	1340	1340	1347	1347	1361	1361	1371	1371	1389	1384	1393	1391	1395	1393	■
-4 3 1	1382	1382	1400	1395	1412	1412	1425	1443	1441	1447	1448	1449	1449	1451	■
-2 3 3	1381	1381	1401	1401	1425	1425	1437	1455	1455	1465	1465	1473	1472	1472	■
-3 4 1	1420	1418	1421	1419	1429	1427	1437	1434	1443	1443	1447	1447	1449	1448	■
3 0 0	1406	1404	1422	1443	1445	1445	1458	1459	1477	1479	1489	1489	1497	1497	■
0 2 4	1407	1407	1430	1458	1455	1455	1475	1499	1497	1507	1506	1506	1508	1508	■
2 1 1	1444	1444	1446	1447	1455	1455	1458	1465	1477	1473	1478	1478	1478	1478	■
1 0 4	1453	1454	1482	1513	1511	1511	1534	1562	1560	1570	1571	1577	1574	1574	■
4 3 0	1476	1476	1487	1484	1502	1500	1515	1511	1525	1525	1533	1533	1537	1537	■
-2 4 3	1528	1528	1554	1554	1547	1560	1559	1575	1572	1572	1579	1577	1577	1577	■
4 4 5	1551	1551	1551	1551	1551	1551	1551	1551	1551	1551	1551	1551	1551	1551	■
-1 3 4	1537	1537	1556	1578	1578	1578	1600	1597	1618	1617	1627	1625	1627	1627	■
-4 1 5	1528	1525	1560	1560	1593	1591	1618	1617	1645	1646	1657	1660	1662	1662	■
-6 0 2	1568	1592	1591	1618	1618	1618	1635	1635	1658	1658	1670	1670	1680	1680	■
-5 2 4	1573	1576	1604	1602	1631	1629	1644	1649	1672	1673	1683	1691	1690	1690	vw

B. The triclinic hexahydrates. The visually estimated powder intensities of the ytterbium and scandium compounds are included.

h k l	Er		Tm		Yb		Lu		I _{obs} Yb		h k l	Sc		I _{obs} Sc
	obs	calc	obs	calc	obs	calc	obs	calc				obs	calc	
1 0 0	70	70	69	70	69	70	70	70	■		1 0 0	74	75	■
0-1 1	145	145	145	145	144	145	147	146	■		0-1 1	149	150	■
0 1 1	156	156	155	157	156	157	156	156	■		0 1 1	160	161	■
1 1-1	166	166	166	167	166	164	167	168	■		1 1-1	174	173	■
1-1 1	200	200	199	200	198	200	199	200	■		1-1 1	201	203	■
1 1 1	252	252	253	253	253	255	255	256	■		1 1 1	267	269	■
1 0-2	262	262	263	263	262	264	263	265	■		1-1 1	273	274	■
1-1 1	262	262	262	262	262	264	263	264	■		1 0-2	279	280	■
0 0 2	267	266	268	268	268	270	270	271	■		0 0 2	333	333	■
2 0 0	278	278	279	280	279	281	280	281	■		2 1-1	349	349	■
2 1-1	326	327	328	328	329	329	330	330	■		2-1 1	394	394	■
0 2 0	333	335	334	335	335	335	335	335	■		2 0-2	421	421	■
2 0-2	397	397	398	398	399	399	-	400	■		1 0 2	445	445	■
1 0 2	411	410	412	413	416	416	418	418	■		2 0 2	526	526	■
1-2 0	428	427	426	427	427	426	427	426	■		0-2 2	599	599	■
2 1 1	489	486	488	490	494	493	497	495	■		1-2-2	652	652	■
2-1 1	519	519	521	522	524	523	-	524	■		1 1-3	657	656	■
1 2-2	553	552	555	554	556	556	556	557	■		3 0 0	672	672	■
5 0 0	625	625	627	626	631	628	630	630	■		3 1-1	672	673	■
1-2-2	-	645	642	643	643	643	-	644	■		0-1 3	713	714	■
2-2 0	-	658	658	659	657	658	656	657	■		3-1-1	735	734	■
3 0-2	-	670	670	673	673	673	675	675	■		2 0 2	752	751	■
0-1 3	665	665	671	670	673	674	677	677	■		1 2 2	782	784	■
1-1-1	-	670	670	672	672	675	678	678	■		2-2-2	809	810	■
2 0 2	692	692	698	698	702	703	705	705	■		1 3-1	814	814	■
2 1-5	699	750	-	705	-	706	708	-	■		0-3 1	840	839	■
0 1 3	701	-	701	-	708	-	712	-	■		1-3-1	896	897	■
2-1-5	778	779	780	781	782	782	784	784	■		1 5 1	930	950	■
0-3 1	804	804	804	804	804	805	805	806	■		3 1 1	930	952	■
1 3-1	-	805	804	804	805	805	806	806	■		1-3 1	946	946	■
1-1 3	858	857	865	865	869	871	872	875	■		3 2 0	955	956	■
5 1 1	-	1247	-	1252	1256	1255	-	1259	■		3-1 1	969	970	■
1 1 3	870	870	876	876	881	882	-	887	■		3 1-3	989	990	■
1-3-1	904	905	903	903	902	902	902	902	■		3-1-3	1072	1073	■
3 2 0	-	895	902	899	902	903	903	907	■		2-2 2	1096	1095	■
1 3 1	-	912	-	913	916	915	-	918	■		2-3-1	1104	1104	■
3-1 1	-	914	920	920	923	922	923	924	■		3-2-2	1118	1117	■
3 2-2	-	916	920	920	923	923	925	926	■		2 0-4	1118	1119	■
3 1-3	926	925	-	929	931	932	934	935	■		4 0 0	1194	1195	■
1-3 1	941	943	-	944	945	944	-	945	■		3 0 2	1206	1207	■
2 3-1	941	941	944	944	945	946	-	948	■		4-1-1	1223	1223	■
1 0-4	986	987	993	992	998	998	1002	1005	■		2-1 3	1276	1276	■
2 2 2	1007	1007	1012	1012	1018	1019	1024	1024	■		2 1 3	1276	1277	■
3 1-3	1025	1027	1030	1029	1028	1029	1032	1031	■		1 2-4	1333	1332	■
4 1-1	-	1065	1072	1071	1074	1074	1081	1077	■		0 4 0	1333	1335	■
3-2-2	1094	1095	1095	1096	1094	1094	1095	1094	■		0-3 5	1347	1347	■
5 0 2	1111	1109	1108	1108	1106	1106	1105	1105	■		2 3-5	1350	1348	■
4-1-1	1165	1165	1170	1169	1169	1169	1170	1170	■		1 4 0	1374	1375	■
2 1 3	1181	1178	1186	1187	1196	1196	1203	1202	■		2 2-4	1374	1374	■
3 0-4	-	1247	-	1252	1256	1255	-	1259	■		1 0 4	1390	1390	■
1 2-4	1251	1253	1258	1260	1267	1267	1272	1271	■		1-2-4	1454	1454	■
2 3-5	1290	1290	1297	1296	1300	1304	1305	1305	■		4 1 1	1489	1487	■
2 2-4	1290	1291	1297	1296	1300	1304	1305	1305	■		3 2 2	1514	1515	■
1 0 4	1283	1282	-	1295	-	1302	1309	1308	■		3 1-3	1573	1573	■
0-3 3	-	1301	-	1306	-	1310	1312	1312	■		4-2-2	1574	1573	■
0 4 0	1341	1342	1342	1341	1341	1341	1342	1341	■		0-4 2	1622	1621	■
4 1 1	1370	1372	1385	1382	1389	1389	1395	1395	■		1 3-3	1667	1666	■
1-2-4	1390	1392	1398	1395	1401	1400	1404	1405	■		0-4-2	1667	1666	■
1-3-3	-	1399	1398	1399	1400	1400	1404	1405	■		3-3-3	1676	1675	■
0 3 5	1408	1407	-	1409	1414	1413	-	1417	■		4 0-4	1686	1685	■
3 2 2	1406	-	1415	1424	1424	-	1431	-	■		1-2 4	1693	1695	■
4-1 1	1448	1448	1459	1458	1462	1461	1465	1464	■					
2-2-4	1474	1474	1480	1476	-	1479	1485	1483	■					
3 3 1	1473	1476	-	1482	1490	1489	1495	1496	■					
3 3 2	1492	1491	1502	1500	1506	1504	1510	1506	■					
3 1-3	1494	1494	1500	1500	1506	1505	1510	1510	■					
1 4-2	-	1512	-	1515	1516	1517	-	1519	■					
1-3 3	1517	1514	-	1521	-	1526	-	1527	■					
2-3-5	-	1530	-	1529	1529	1528	1531	1530	■					
4-2-2	-	1530	-	1530	1532	1528	1531	1530	■					
1 3 3	1557	1554	1562	1559	1565	1565	1571	1572	■					
0-4 2	1561	1561	1562	1563	1565	1565	1565	1565	■					
4 0-4	1590	1586	1592	1591	1593	1593	1601	1599	■					

Table 2. Observed and calculated structure factors of YBOx.

The 102 reflections not obeying the condition

$0.80 \leq |E_o|/|E_c| \leq 1.25$ are denoted by asterisks.

h=12 k=0	h=8 k=2	9 70 62	0 72 78	-5 158 124*	7 111 112	4 104 140	h=3 k=5
4 65 70	0 55 59	4 2 27 42*	4 2 27 42*	-3 71 54*	11 65 67	6 63 36	-7 112 101
h=11 k=0	h=6 k=4	h=6 k=4	4 127 124	4 127 124	h=0 k=2	8 62 48*	-5 171 127*
0 50 51	0 141 142	-4 81 81	8 131 121	1 173 175	h=0 k=2	10 64 70	-3 87 113*
2 62 37	0 114 110	-4 81 83	8 81 78	5 115 193	-10 84 77		1 105 89
4 77 60*	0 91 89	-2 43 38	5 116 128	-8 168 137	h=2 k=1		3 127 97*
h 34 33	1 65 61	2 112 106	h=4 k=5	9 52 49	-10 159 141	-11 76 63	5 127 96*
		4 104 95	-5 71 54*	2 61 77	-2 160 135	-5 210 186	h=4 k=0
h=11 k=1	h=8 k=3	6 67 65	-1 121 126	h=2 k=4	6 81 92	-3 108 169	2 145 116*
-1 59 34	-5 95 86	8 40 38	1 138 144	h=2 k=2	8 148 139	-1 178 188	4 216 209
5 65 55	-3 92 99	10 29 43*	5 117 112	h=0 k=1	10 71 85	-1 140 124	6 116 101
7 68 65	-1 58 62		7 93 79	-4 180 141*		3 148 132	
h=11 k=2	h=6 k=5	h=6 k=5	9 93 85	-2 142 133	h=0 k=3	5 90 92	h=4 k=1
0 44 48	5 142 126	-5 51 45	0 165 191	-11 51 56	-7 27 59	7 98 95	-11 76 79
2 88 73	0 72 72	-1 93 96	h=3 k=0	4 58 59	-5 258 174*	9 59 65	-7 146 142
4 57 34	h=8 k=4	h=10 k=1	2 150 188*	6 84 88	-3 248 181*	h=2 k=2	-3 93 125*
	0 120 114	5 54 47	4 131 135	8 94 95	-1 74 85	-10 74 55*	-1 231 217
h=11 k=3	h=6 k=6	7 103 67	0 103 88	10 49 50	5 191 176	-4 128 107	1 432 208
-1 11 30*	4 55 57	0 60 76*	10 74 80	h=2 k=3	5 180 182	-6 170 145	3 90 95
1 34 32	6 66 67	12 60 58		7 121 116	-4 188 148*	5 56 49	
3 31 29				-9 76 68	11 35 35	7 94 82	7 113 101
5 40 47	h=4 k=5	h=5 k=0	h=3 k=1	7 71 77	h=0 k=4	4 124 115	9 65 87
	-3 48 73	-5 142 183	-5 148 137	-5 174 117*			
h=10 k=0	-1 74 76	4 78 84	-3 248 211	-3 94 72*	-8 174 121	6 45 42	h=4 k=2
0 67 37	3 51 48	8 127 114	-1 152 145	-1 40 42	-6 114 99	5 57 57	-12 65 70
6 79 74	1 54 51	17 100 90	5 104 100	-2 34 33	10 53 95	10 53 95	-2 116 123
h 74 59	7 97 146	3 170 162	3 170 162	3 115 119	-2 147 157		-0 159 152
		5 184 190	5 184 190	5 134 117	2 206 195	h=2 k=3	-4 176 210
h=10 k=1	h=7 k=0	-5 180 135*	7 127 147	9 61 58	4 74 75	-11 98 93	-2 120 145
3 106 89	0 102 132	-3 143 139		h=1 k=0	6 56 61	-8 167 168	2 120 145
5 80 72	0 72 77	1 60 73	-3 178 171	h=3 k=2	8 106 103	-5 150 124*	6 173 153
	0 72 77	3 170 140	-8 163 122*	0 137 141	10 73 73	-3 240 194*	6 105 90
h=10 k=2	h=7 k=1	5 161 165	-4 127 86*	4 204 200	h=0 k=5	-1 137 160	h=4 k=3
-2 69 62	h=7 k=1	11 69 73	-2 118 81*	4 184 185	-7 84 71	3 80 77	-11 60 67
0 77 74	h=7 k=1	h=5 k=2	2 291 211	10 63 67	-5 163 129*	5 123 111	-9 121 117
2 51 32	-1 67 70	-8 49 50	4 62 71	12 60 63	-3 154 137*	7 111 114	-7 108 122
6 50 44	-1 77 73	-2 150 136	8 80 81	h=1 k=1	-1 59 89*	9 60 68	-1 235 229
h 58 54	-1 77 81	0 160 127	10 119 107	h=1 k=1	5 150 149		-1 235 229
h=10 k=3	h=7 k=2	2 94 100	12 52 55	-11 117 69*	5 144 112*	h=2 k=4	1 212 195
1 44 47	h 88 80	6 94 80		h=0 k=6	7 111 99	-10 53 54	3 62 59
3 93 44	11 79 69	8 163 150	h=3 k=3	-7 69 85	-5 153 131	-8 94 122	7 110 104
5 70 58		10 92 82	-5 52 50	-3 153 135	h=1 k=2	-4 129 117	5 65 83
	h=7 k=2	h=5 k=0	h=5 k=0	-1 364 244*	2 161 129	-4 93 87	
h=10 k=4	-4 133 126	h=5 k=3	-3 195 145*	4 203 222*	4 203 222*	-4 29 69	h=4 k=4
0 45 46	-2 105 112	5 121 90*	-1 252 192*	3 42 44	6 151 160	2 167 168	-10 44 35
6 47 51	4 89 68	-3 179 134*	1 53 50	5 57 60	8 73 81	4 148 140	-8 50 50
	4 133 122	1 58 65	3 151 144	7 120 147	6 59 55	-6 59 55	-6 103 100
h=10 k=5	h 136 129	3 111 113	5 114 118	9 130 141	h=1 k=3	h 48 54	-4 113 144*
1 31 35	h 96 81	5 145 145	7 133 125	-9 140 130	-7 150 131	h=2 k=5	-2 61 52*
3 56 63	h=7 k=3	11 50 54	11 34 33	-6 187 135*	-5 69 69	-4 0 49*	4 150 124*
5 54 63	h=5 k=0	h=5 k=0	h=5 k=0	-8 0 79	-3 89 78	-5 150 113*	6 111 99
h=9 k=0	h=5 k=0	h=5 k=0	h=5 k=0	2 116 120	-1 214 220	-3 153 143	8 37 40
2 67 76	-1 69 76	-2 93 98	-8 122 111	4 254 251	6 150 160	-8 150 160	
h 81 84	1 94 93	0 114 120	-6 114 98	6 50 60	3 133 129	-1 53 57	h=4 k=5
6 99 82	5 133 152	2 118 127	-4 86 70	10 52 54	7 68 66	3 37 38	-9 94 87
10 37 57	4 58 60	5 51 48	-2 47 47	h=1 k=4	5 87 100	5 134 93*	-1 147 155
	h=7 k=4	11 117 112	0 157 153	h=1 k=5	11 74 76	7 81 81	1 147 156
h=9 k=1	h=7 k=4	10 61 60	2 147 155	-11 56 54	-9 80 80	h=1 k=6	3 55 40
-3 53 40*	-4 86 94	h=5 k=4	4 107 114	-9 80 80	-10 87 78	h=3 k=0	7 71 78
-1 60 64	-2 86 93	h=5 k=5	6 47 52	-7 103 88	-10 87 78	-2 108 132*	
1 124 117	-1 97 94	h=5 k=6	10 93 96	-5 142 142*	5 53 48	4 85 60	h=5 k=0
7 82 73	4 92 85	-5 105 90	5 1 253 278	-2 292 204*	4 271 217	6 101 93	2 117 121
9 114 99*	h 93 95	-3 102 103	h=3 k=5	-2 292 204*	4 271 217	8 141 127	4 49 49
	h 65 62	3 143 125	-5 107 99	5 1 253 278	4 271 217	10 67 55	8 60 60
h=9 k=2	h=7 k=5	3 120 120	5 179 150	7 84 81	4 214 172	h=3 k=1	7 135 134
-4 82 71	h=7 k=5	7 57 54	-1 154 120	7 84 81	4 214 172	h=3 k=2	-7 135 134
2 67 68	-5 53 59	h=4 k=6	1 31 34	5 107 114	6 143 150	h=3 k=3	-3 153 171
4 122 116	1 83 96	h=4 k=7	3 93 93	11 51 49	8 57 65	h=3 k=4	-1 70 72
6 69 69	3 167 111	h=4 k=8	4 209 212	7 117 111	h=1 k=7	-1 70 72	-3 154 160
h=9 k=3	h=5 k=0	h=4 k=9	9 60 58	9 60 58	h=1 k=8	-1 70 72	-3 154 160
-3 33 34	h=6 k=0	h=4 k=10	12 84 78	12 84 78	h=1 k=9	-1 70 72	-3 154 160
-1 79 72	h=6 k=1	h=4 k=11	h=2 k=0	h=2 k=0	h=1 k=10	-1 70 72	-3 154 160
1 105 109	h=6 k=2	h=4 k=12	h=2 k=1	h=2 k=1	h=1 k=11	-1 70 72	-3 154 160
3 47 47	h=6 k=3	h=4 k=13	h=2 k=2	h=2 k=2	h=1 k=12	-1 70 72	-3 154 160
7 57 54	h=6 k=4	h=4 k=14	h=2 k=3	h=2 k=3	h=1 k=13	-1 70 72	-3 154 160
9 85 89	h=6 k=5	h=4 k=15	h=2 k=4	h=2 k=4	h=1 k=14	-1 70 72	-3 154 160
h=9 k=4	h=6 k=6	h=4 k=16	h=2 k=5	h=2 k=5	h=1 k=15	-1 70 72	-3 154 160
-2 50 55	h=6 k=7	h=4 k=17	h=2 k=6	h=2 k=6	h=1 k=16	-1 70 72	-3 154 160
2 43 42	h=6 k=8	h=4 k=18	h=2 k=7	h=2 k=7	h=1 k=17	-1 70 72	-3 154 160
4 84 83	h=6 k=9	h=4 k=19	h=2 k=8	h=2 k=8	h=1 k=18	-1 70 72	-3 154 160
6 81 55	h=6 k=10	h=4 k=20	h=2 k=9	h=2 k=9	h=1 k=19	-1 70 72	-3 154 160
h=9 k=5	h=6 k=11	h=4 k=21	h=2 k=10	h=2 k=10	h=1 k=20	-1 70 72	-3 154 160
-1 193 154	h=6 k=12	h=4 k=22	h=2 k=11	h=2 k=11	h=1 k=21	-1 70 72	-3 154 160
h=9 k=6	h=6 k=13	h=4 k=23	h=2 k=12	h=2 k=12	h=1 k=22	-1 70 72	-3 154 160
-1 60 60	h=6 k=14	h=4 k=24	h=2 k=13	h=2 k=13	h=1 k=23	-1 70 72	-3 154 160
1 76 79	h=6 k=15	h=4 k=25	h=2 k=14	h=2 k=14	h=1 k=24	-1 70 72	-3 154 160
3 44 42	h=6 k=16	h=4 k=26	h=2 k=15	h=2 k=15	h=1 k=25	-1 70 72	-3 154 160
7 37 42	h=6 k=17	h=4 k=27	h=2 k=16	h=2 k=16	h=1 k=26	-1 70 72	-3 154 160
h=9 k=7	h=6 k=18	h=4 k=28	h=2 k=17	h=2 k=17	h=1 k=27	-1 70 72	-3 154 160
h=9 k=8	h=6 k=19	h=4 k=29	h=2 k=18	h=2 k=18	h=1 k=28	-1 70 72	-3 154 160
h=9 k=9	h=6 k=20	h=4 k=30	h=2 k=19	h=2 k=19	h=1 k=29	-1 70 72	-3 154 160
h=9 k=10	h=6 k=21	h=4 k=31	h=2 k=20	h=2 k=20	h=1 k=30	-1 70 72	-3 154 160
h=9 k=11	h=6 k=22	h=4 k=32	h=2 k=21	h=2 k=21	h=1 k=31	-1 70 72	-3 154 160
h=9 k=12	h=6 k=23	h=4 k=33	h=2 k=22	h=2 k=22	h=1 k=32	-1 70 72	-3 154 160
h=9 k=13	h=6 k=24	h=4 k=34	h=2 k=23	h=2 k=23	h=1 k=33	-1 70 72	-3 154 160
h=9 k=14	h=6 k=25	h=4 k=35	h=2 k=24	h=2 k=24	h=1 k=34	-1 70 72	-3 154 160
h=9 k=15	h=6 k=26	h=4 k=36	h=2 k=25	h=2 k=25	h=1 k=35	-1 70 72	-3 154 160
h=9 k=16	h=6 k=27	h=4 k=37	h=2 k=26	h=2 k=26	h=1 k=36	-1 70 72	-3 154 160
h=9 k=17	h=6 k=28	h=4 k=38	h=2 k=27	h=2 k=27	h=1 k=37	-1 70 72	-3 154 160
h=9 k=18	h=6 k=29	h=4 k=39	h=2 k=28	h=2 k=28	h=1 k=38	-1 70 72	-3 154 160
h=9 k=19	h=6 k=30	h=4 k=40	h=2 k=29	h=2 k=29	h=1 k=39	-1 70 72	-3 154 160
h=9 k=20	h=6 k=31	h=4 k=41	h=2 k=30	h=2 k=30	h=1 k=40	-1 70 72	-3 154 160
h=9 k=21	h=6 k=32	h=4 k=42	h=2 k=31	h=2 k=31	h=1 k=41	-1 70 72	-3 154 160
h=9 k=22	h=6 k=33	h=4 k=43	h=2 k=32	h=2 k=32	h=1 k=42	-1 70 72	-3 154 160
h=9 k=23	h=6 k=34	h=4 k=44	h=2 k=33	h=2 k=33	h=1 k=43	-1 70 72	-3 154 160
h=9 k=24	h=6 k=35	h=4 k=45	h=2 k=34	h=2 k=34	h=1 k=44	-1 70 72	-3 154 160
h=9 k=25	h=6 k=36	h=4 k=46	h=2 k=35	h=2 k=35	h=1 k=45	-1 70 72	-3 154 160
h=9 k=26	h=6 k=37	h=4 k=47	h=2 k=36	h=2 k=36	h=1 k=46	-1 70 72	-3 154 160
h=9 k=27	h=6 k=38	h=4 k=48	h=2 k=37	h=2 k=37	h=1 k=47	-1 70 72	-3 154 160
h=9 k=28	h=6 k=39	h=4 k=49	h=2 k=38	h=2 k=38	h=1 k=48	-1 70 72	-3 154 160
h=9 k=29	h=6 k=40	h=4 k=50	h=2 k=39	h=2 k=39	h=1 k=49	-1 70 72	-3 154 160
h=9 k=30	h=6 k=41	h=4 k=51	h=2 k=40	h=2 k=40	h=1 k=50	-1 70 72	-3 154 160
h=9 k=31	h=6 k=42	h=4 k=52	h=2 k=41	h=2 k=41	h=1 k=51	-1 70 72	-3 154 160
h=9 k=32	h=6 k=43	h=4 k=53	h=2 k=42	h=2 k=42	h=1 k=52	-1 70 72	-3 154 160
h=9 k=33	h=6 k=44	h=4 k=54	h=2 k=43	h=2 k=43	h=1 k=53	-1 70 72	-3 154 160
h=9 k=34	h=6 k=45	h=4 k=55	h=2 k=44	h=2 k=44	h=1 k=54	-1 70 72	-3 154 160
h=9 k=35	h=6 k=46	h=4 k=56	h=2 k=45	h=2 k=45	h=1 k=55	-1 70 72	-3 154 160
h=9 k=36	h=6 k=47	h=4 k=57	h=2 k=46	h=2 k=46	h=1 k=56	-1 70 72	-3 1

$= 13.3^\circ$ was used in the correction for the polarization effects. The transmission factor evaluated by numerical integration, varied in the interval 0.696 - 0.810.

Full matrix least squares refinement minimizing $\sum w(|F|_O - |F|_C)^2$ were performed with weights $w = 1/(\sigma_C^2 + a|F|_O^2 + b)$. In the last cycles of refinement $a = 0.00003$ and $b = 2.0$ were used. The convergency was followed by the agreement indices R and wR defined by $R = \sum ||F|_O - |F|_C| / \sum |F|_O$ and $wR = [\sum w(|F|_O - |F|_C)^2 / \sum w|F|_O^2]^{1/2}$. A refinement of the scale factor and the positional parameters for the non-hydrogen atoms with anisotropic thermal parameters converged to $R = 0.043$ and $wR = 0.048$. The hydrogen atoms were then located in a difference electron density map, which was calculated using data with $\sin\Theta/\lambda < 0.5$. The map indicated two different orientations for the water molecule O(8). Thus the hydrogen atoms of O(8) are distributed among four positions. One of these positions belongs to a hydrogen bond O(8)-O(8) as described on p. In the refinement hitherto performed the temperature factors of the hydrogen atoms have been given a fictitious value of $5.0 \text{ \AA}^2$. This refinement converged to $R = 0.035$ and $wR = 0.038$. The average values of $w(|F|_O - |F|_C)^2$ were nearly constant in different $|F|_O$ intervals. The value of S, defined by $S = [\sum w(|F|_O - |F|_C)^2 / (m - n)]^{1/2}$, where m is the number of observations and n is the number of parameters varied, was 0.97. The atomic coordinates thus refined are given in Table 1.

Table 1. Atomic parameters with estimated standard deviations in S₂O₃. R₁, R₂, and R₃ are the root mean square components along the principal axes of the ellipsoids of thermal vibration. The occupancy of the positions H(5), H(6), H(7), and H(8) is 0.5.

Atom	$x \cdot 10^4$	$y \cdot 10^4$	$z \cdot 10^4$	$R_1/\text{\AA}$	$R_2/\text{\AA}$	$R_3/\text{\AA}$
Sc	3071.5(5)	33.0(6)	1931.4(5)	0.089(1)	0.099(1)	0.135(1)
O(1)	1678(2)	-442(2)	-411(2)	0.110(4)	0.138(4)	0.193(3)
O(2)	681(2)	357(2)	1886(2)	0.117(4)	0.144(4)	0.181(3)
O(3)	4009(2)	1526(2)	640(2)	0.120(4)	0.135(4)	0.168(3)
O(4)	4522(2)	-1558(2)	862(2)	0.124(4)	0.134(3)	0.139(3)
O(5)	5466(2)	96(2)	3361(2)	0.116(4)	0.135(3)	0.152(3)
O(6)	3072(2)	9(2)	4304(2)	0.111(4)	0.136(4)	0.183(3)
O(7)	2687(3)	2687(3)	2602(3)	0.127(4)	0.153(4)	0.209(3)
O(8)	250(4)	-1636(5)	4381(5)	0.185(4)	0.239(5)	0.327(5)
O(9)	2498(2)	-2404(2)	2159(2)	0.141(4)	0.152(4)	0.175(3)
C(1)	285(3)	-233(3)	-668(3)	0.123(5)	0.135(5)	0.148(5)
C(2)	4846(3)	898(3)	-66(3)	0.103(6)	0.139(5)	0.141(5)
C(3)	5699(3)	22(3)	4737(3)	0.115(5)	0.136(5)	0.140(5)
H(1)	-3183(54)	1808(56)	2733(55)			
H(2)	-2361(53)	1967(56)	1943(55)			
H(3)	-1721(56)	-2351(56)	3236(55)			
H(4)	-3074(55)	-1996(56)	2986(55)			
H(5)	298(130)	-804(154)	3994(119)			
H(6)	313(144)	-806(150)	4604(146)			
H(7)	1373(108)	-1468(111)	4095(105)			
H(8)	965(108)	-1594(109)	5441(113)			

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